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MINERALOGY OF URANIUM*

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I

At the present time approximately 70 different minerals are known that contain uranium as an essential constituent. Only a very few of these minerals are important as ores of the element. At the time of the discovery of the element uranium by Klaproth in 1789 only two uranium minerals were known, torbernite, and a mineral, pitchblende, for which the name uraninite is now appropriate. Both of these species had been recognized as distinct entities long before by the miners of Saxony and Bohemia. Torbernite and its analogue autunite were first set forth as clearly defined species in 1823. By 1850 the number of uranium minerals had grown to 6; and by 1900 roughly one-third of the species now known had been recognized.

Advances in the mineralogy of uranium have markedly reflected the discovery of new deposits and of new uses of the element. The application of uranium as a pigmenting material in glass and ceramics toward the middle of the 19th Century inaugurated the mining of uraninite in the Erzgebirge. This activity was accompanied by numerous studies of uranium minerals, chiefly by Austrian and German investigators. Among them may be mentioned Albin Weisbach, who alone described 7 new species. Another period of active research on the mineralogy and geology of uranium accompanied the discovery of radioactivity by Becquerel in 1896 and the isolation of radium by the Curies and Bémont in 1898. The uranium deposits of the Colorado Plateau were first explored and exploited at this time, following the description of the important ore mineral carnotite by Friedel and Cumenge in 1899. The mineralogy of the

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Plateau uranium and vanadium ores was studied during this period by W. F. Hillebrand and F. L. Hess, among others.

Following the discovery of the mineralogically diverse uranium ores of the Belgian Congo in 1915, a large number of new uranium minerals were described. This work was done chiefly by Belgian mineralogists, among whom may be mentioned H. Buttgenbach, J. Thoreau, J. Mélon and, in particular, Alfred Shoep. Shoep described 12 of the 24 uranium minerals discovered in the Belgian Congo. No such flood of new species attended the discovery of the rich deposit at Great Bear Lake in 1930, owing primarily to the very small extent of surface oxidation at that place.

The discovery of atomic fission in 1937 by Hahn and Strassmann was followed by a great program of work on the uses of uranium and of the trans-uranium elements both as military weapons and as sources of power. This work brought about a large and immediate demand for uranium ores that still continues, and gave a great impetus to the study of the geology, geochemistry, and mineralogy of uranium. It is largely with these recent studies that I shall be concerned here.

II

Until very recently, uranium minerals as a group were very poorly characterized. In many instances, particularly with less common minerals described before about 1880, it was virtually impossible to recognize the mineral with certainty from the existing published information. A few species described in recent years also fall into this category. The difficulties in part stemmed from inadequacies of the older analytical work and, more generally, from the occurrence of the minerals in relatively small amount as very fine-grained aggregates and mixtures.

It was in fact found useful in the past to use a generic term, gummite, to designate various uranium minerals, found chiefly as oxidation products of uraninite, whose true identity was unknown. The term gummite, like its analogues wad and limonite, found its widest use in the days before the advent of *x*-ray diffraction and other techniques suited to the study of fine-grained mixtures. Of the dozen or so uranium minerals that are now known to constitute the traditional gummite, only one species, the silicate uranophane, was known prior to 1890, although all of these minerals had been examined in the form of gummite, if not identified, by the early mineralogists.

In the past seven or eight years, virtually the whole mineralogy of uranium has been re-examined and the known species provided with definitive redescriptions. A particularly profitable approach in this work has been the study of synthetic material, prepared in bulk in pure form and shown to be identical with the natural mineral in question. Large use also has been made of *x*-ray and electron diffraction techniques. *X*-ray powder data offer a convenient and positive means of identification of these minerals, and sometimes are indispensable. One of the first objectives of the work was the preparation of a complete file of standard *x*-ray patterns. A list of *d*-spacings for the known species has since been published. Crystal structure studies also have been fruitful. The resolution of some of the standing problems in this field, such as the chemistry and mineralogy of the hydrated uranyl oxides containing lead or other cations, and problems of the uranyl sulfates, is dependent on structural studies. In recent years the U. S. Geological Survey has very profitably carried on structural studies of uranium and vanadium minerals in conjunction with studies of the solution-chemistry of these elements, particularly with regard to complex-formation in solution.

A key problem in the general program has been the procuring of authentic and preferably type specimens for the redefinition of ill-defined species. One of the first steps taken was the preparation by the Trace Elements Laboratory of the U. S. Geological Survey, in 1951, of an inventory of the specimens of uranium minerals contained in the leading reference mineral collections of the United States. It was then found that about 10 per cent of the known species and significant varieties of uranium minerals were not represented by authentic specimens in this country. This deficiency has since been remedied, but after much difficulty. It should be emphasized in this connection that the science of mineralogy in its descriptive aspects is a specimen-science, like botany and entomology, and requires for its practice and progress the preservation and ready availability of type material. Mineralogists who describe new species or significant varieties of known species should ensure that specimens are preserved in the leading reference mineral collections of the world.

This program of work on the mineralogy of uranium was essentially a cooperative effort carried on at a relatively few laboratories in this country. These laboratories included the Trace Elements Laboratory of the U. S. Geological Survey in Washington, the Denver and Grand Junction laboratories of the Atomic Energy Commission and the Survey, Professor Gruner's group at Minnesota, Professor Kerr's group at Columbia, and the Harvard group. Most of the university work was supported by contracts with the Atomic Energy Commission.

Much of this mineralogical research centered about the Trace Elements Laboratory, and brief mention may be made of the work of this organization. The Trace Elements Laboratory was created in 1947 as a unit under the Geochemistry and Petrology Branch of the Geological

Survey. It is supported by funds transferred by the Atomic Energy Commission, which, by statute, has the primary responsibility for the whole program of work on fissionable raw materials. A broadly inclusive but well integrated organization, that at its peak employed about 130 scientific personnel, it carries on laboratory investigations on the mineralogy, chemistry, petrography, geochemistry and nuclear physics of natural radioactive substances. Most of the research done by the Laboratory has been made publically available; of some 270 official research reports made to date, 32 already have been published as Bulletins or Professional Papers of the Geological Survey, and 109 have appeared in scientific periodicals. As one of its duties, the laboratory makes chemical or spectrographic analyses together with radiometric and, in part, *x*-ray or other study of field samples originating in other branches of the Geological Survey. A total of over one-third of a million such samples have been examined to date. In addition, more or less radioactive samples submitted by the general population have been examined in very large numbers by this and other Government laboratories.

Contributions to the mineralogy of uranium during this general period also were made by a few laboratories in foreign countries. Here may be mentioned work in Canada at the University of Toronto, Queen's University and the Geological Survey, and at establishments of the Atomic Energy Commissions of France and of Great Britain. The Russian contributions to this field are known only from a few recent papers descriptive of new species.

A detailed summary account of the mineralogy of uranium and thorium is in press as a Bulletin of the U. S. Geological Survey.

III

Many problems in the descriptive and interpretive mineralogy of uranium still remain. I shall outline a few of these problems, but first I will briefly characterize the mineralogy of this element in crystallochemical terms.

Uranium occurs in two geologically stable valence states: the four-valent or uranous state, and the six-valent state. In the latter state, the uranium forms a cationic complex-ion, the so-called uranyl ion, composed of a linear group of two oxygen ions with the six-valent uranium ion held between them. This complex ion has a net positive charge of two units. The coordination number with oxygen of the six-valent uranium ion ordinarily is six or eight in different compounds, and the uranyl configuration appears as a distortion of this coordination in which two of the surrounding oxygen ions, diametrically opposed to the central uranium ion, are more closely bound thereto than are the other oxygens of the coordination group. The uranyl ion is readily complexed in both carbonate and sulfate solutions. The carbonate and sulfate complexes are relatively easily reduced into less soluble uranous compounds, including uranium dioxide and hydrated uranous oxides, and these complexes doubtless play an important role in the transport and deposition of uranium in nature.

All but two of the 70 or so known uranium minerals contain the uranyl ion. All are secondary minerals. It is interesting to note that the mineralogy of the uranyl ion stands quite alone. There are no analogues of these minerals among the minerals formed by other elements. This is due to the unusual dumbbell-like shape of the uranyl ion, which finds no counterpart among the ions of other elements. It is for this same reason that the uranyl ion does not occur in significant amounts as a vicarious constituent in other minerals. The solid solution series in which uranyl compounds do enter in general involve substitution for either the other cations that may be present in the crystal structure or of the anions. The thermal instability of the uranyl ion is an added factor that weighs against its entrance in solid solution into high-temperature igneous and metamorphic minerals.

All this contrasts with the mineralogy of the four-valent or uranous ion. This ion acts as a sphere in crystallochemical regards, with a radius of about 1 Angstrom. The mineralogy of this ion, unlike that of the uranyl ion, has structural analogies with the mineralogy of other elements of the same valence and of comparable ionic radius. Here may be mentioned thorium, zirconium and four-valent cerium. This relation is shown by the nesosilicates of the zircon group, by their hydroxyl-containing analogues of the thorogummite group, and by the fluorite-type dioxides of the uraninite group. Partial or complete solid solution series extend between these isostructural species. The four-valent uranium ion, again in contrast with the uranyl ion, commonly occurs in significant amounts as a vicarious constituent in other minerals. Because of its high valence and relatively large size, however, it is not found in large amounts in substitution for the common cations of rock-forming minerals. The small substitution of four-valent uranium for calcium in apatite, however, is of economic interest because it can be recovered as a by-product. Other minerals in which four-valent uranium occurs as a vicarious constituent that are of interest as sources of uranium include pyrochlore-microlite, brannerite and betafite. In these minerals, coupling mechanisms are available for the housing in solid solution of large, polyvalent ions. Virtually the whole production of uranium, however, presently comes from minerals in which uranium is an essential constituent. Quite the opposite is true of thorium. Monazite, the ore mineral of thorium, contains this element in solid solution in substitution for cerium and lanthanum.

URANINITE

A great deal of attention has been given to uraninite in recent years, since this is the most important ore mineral of uranium. It is surprising that this long-known mineral, certainly now one of the most important natural substances known to man, should be so little understood. The problem of the chemical composition of uraninite plagued chemists for over 125 years. It still does. The mineral was early considered to have the composition U_3O_8 or U_2O_5, or to be an orthouranate of uranium and lead. W. F. Hillebrand in his definitive analytical study of uraninite made in the period 1888–1892 disproved these ideas, but could reach no definite interpretation of the composition himself. The problem was largely resolved by Goldschmidt and Thomassen in 1923, when they showed that the crystal structure of the mineral was of the calcium fluoride type and that its ideal chemical composition, at least, was uranium dioxide, UO_2. The presence of variable and often large amounts of six-valent uranium in the mineral, a puzzling feature that was chiefly responsible for the failure of the earlier interpretations, was ascribed to a non-stoichiometric variation in composition. In this, it was proposed that the six-valent uranium substituted for the normal four-valent uranium ions of the structure, and that valence compensation was effected by the coupled entrance of oxygen ions into vacant interstitial positions. The possibility of intimate admixture of amorphous uranium trioxide, however, cannot be excluded.

This problem of the composition and structure of uraninite requires further study. The mechanism by which the lead atoms formed by radioactive decay are housed within the structure is still not understood, and the coordination with oxygen of any six-valent uranium ions present is an associated problem. If the six-valent uranium ions tend to assume a uranyl configuration, as one might suppose, then this would require a distortion of the normal oxygen coordination. The existence of this distortion and its consequences in natural material have yet to be investigated. It may account for the differences in habit between uraninite and so-called pitchblende. In the synthetic tetragonal phase in the composition range $UO_{2.2}$ to $UO_{2.3}$ structural strain apparently is relieved by a linear arrangement of the uranyl configuration. The entrance of oxygen ions into a vacant position that itself is completely bounded by oxygen ions violates a fundamental rule of crystal chemistry.

Further, are the extra oxygen ions distributed through the uraninite structure in a random way or with order? Laboratory study has shown that ordering of the oxygen positions is an important mechanism in the anhydrous system UO_2-UO_3, and that this ordering is accompanied by a variety of phase changes that can be followed by *x*-ray means. Strangely, none of the phases that occur in synthetic anhydrous material have been identified in natural material that covers essentially the same range of composition. There is some recent evidence, obtained by study of changes in the unit cell dimensions produced by annealing, that the low temperature uranitite of the sandstone deposits of the Colorado Plateau and of hydrothermal veins may be ordered. There also is the possibility, particularly in the older uraninites, that order originally present among the extra oxygens may have been later destroyed by self-irradiation—a partial metamictization of the structure. The ordered oxide U_4O_9 may come into consideration here.

There is a further problem with uraninite that has important geological implications. It has been generally supposed, since the work of Goldschmidt and Thomassen, that uraninite was originally deposited in nature as unoxidized uranium dioxide, and that the content of six-valent uranium and extra oxygen of the mineral is due to secondary oxidation and weathering. Secondary oxidation unquestionably can and does happen. But it also is true that uraninite can crystallize directly from solution in a more or less oxidized condition. Oxidized uraninite has been synthesized in the laboratory by hydrothermal means over a wide range of temperature. The amount of initial oxidation in general increases with decreasing temperature of synthesis; and also is influenced by the reducing power and pH of the solution. It is in fact difficult to obtain wholly unoxidized material by hydrothermal means. This matter is of interest in connection with recent efforts to use the cell edge of uraninite as a means of age determination.

Increasing oxidation is accompanied by a decrease in the unit cell dimensions. Study by *x*-ray methods of some 300 samples of uraninite from world-wide localities indicates that low temperature natural uraninite, such as that of the Colorado Plateau, has relatively small unit cell dimensions; middle-temperature uraninite, such as that from hydrothermal veins, has an intermediate range of cell dimensions; high temperature uraninite, such as that of pegmatites, when corrected for the content of thorium and rare-earths usually present, has the largest cell dimensions. This correlates with the laboratory observations on initial oxidation as a function of temperature. It also is significant in this connection that no natural uraninite has yet been described that is wholly unoxidized. The smallest content of six-valent uranium so far reported corresponds to the formula $UO_{2.15}$. Interesting problems thus remain with uraninite, and there is no doubt but that their study will contribute to a further understanding of the geochemistry of uranium.

URANIUM SILICATES

The recent description of coffinite, a silicate of four-valent uranium that is widespread in the unoxidized uranium deposits of the Colorado Plateau, is of interest in connection with the crystal chemistry of the zircon family of minerals. Coffinite is isostructural with zircon. Study of pure, coarsely crystallized material would be desirable, if such material can be found. The available evidence, however, indicates that a considerable part of the (SiO_4) groups of this nesosilicate have been substituted by hydroxyl ions in groups of four. This mechanism of compositional variation is already well-known in the so-called hydrogarnets.

It now appears that the zircon family of minerals may fall into two groups. The zircon group proper includes the anhydrous minerals $ZrSiO_4$ (zircon), $ThSiO_4$ (thorite), and the hypothetical but crystallochemically possible substances $USiO_4$ and $CeSiO_4$. The two known members are high-temperature, primary minerals. Parallel to each of these known or hypothetical minerals there apparently exist hydroxyl-containing variants. These form at low temperatures, and in part are secondary minerals. This group of minerals, for which the name Thorogummite Group would be appropriate, seemingly includes coffinite as the variant of hypothetical $USiO_4$, thorogummite as the variant of thorite, cyrtolite as the variant of zircon, and possibly the ill-defined mineral freyalite as the variant of hypothetical $CeSiO_4$. The hydroxyl-containing variants of both zircon and thorite have been synthesized hydrothermally at temperatures as low as 150° C., and the content of hydroxyl has been verified by infra-red absorption studies. It also has proven possible to recrystalize metamict zircon and thorite by hydrothermal means at moderate temperatures. Apparently this also happens in nature. Further studies of the crystal chemistry of the zircon family would be highly desirable, particularly of zircon itself in view of the use of this mineral in age-determination work.

I have outlined here only a few of the more interesting or more profitable problems that exist in this general field. There are others. In conclusion, I do not wish to convey the impression that these are residual problems, whose resolution will leave clear this small part of our science. It has been said, the greater the sphere of our knowledge, the larger the circumference of our ignorance.

ELECTRON DIFFRACTION STUDIES OF SERPENTINE MINERALS*

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ABSTRACT

Electron microscope and single crystal electron diffraction methods have been used to examine the morphology and unit cell parameters of the serpentine minerals, and their inter-relations. Single tubular elements of silky chrysotile give electron diffraction patterns of clino- or ortho-chrysotile similar to the *x*-ray fibre diagrams; the two types are seen to exist in separate strands. Splintery varieties have a less disordered layer stacking than do silky fibres.

Massive serpentines giving the lizardite *x*-ray powder pattern are found to be essentially platy; two bastites give an electron diffraction pattern similar to that of lizardite from Kennack Cove.

Antigorites and picrolites are seen to be structurally similar giving characteristic superlattice spot patterns. The *a* parameter of antigorites can vary from one crystal to another and takes on "preferred" values.

A synthetic Mg-Ge serpentine and a serpentine from Unst, Shetlands, possess a 6-layered ortho cell. Comment is made on nomenclature of certain serpentine varieties.

INTRODUCTION

Much detailed *x*-ray diffraction work has been devoted to the elucidation of the crystal structures of the serpentine minerals and especially of chrysotile and antigorite. It is now generally accepted that both minerals have layer structures closely similar to that of kaolinite but with a trioctahedral Mg layer replacing the dioctahedral Al layer.

In the case of chrysotile, the fundamental layers may be curved so as to form hollow tubes or rolls. Electron micrographs of dispersed material have been interpreted as showing a tubular morphology (Turkevich and Hillier (1949); Bates, Sand and Mink (1950); Noll and Kircher, (1951)). The detailed analyses by Whittaker (1954, 1955*a*, 1955*b*) and by Jagodzinski and Kunze (1954) show a close similarity between the diffraction effects to be expected from cylindrical lattices and those obtained experimentally. On the other hand, Pundsack (1956) has shown that the measured density of compact bundles of chrysotile fibres is incompatible with both tubular and solid cylindrical formations. It may be that the *x*-ray data can be interpreted in terms of compact bundles of curved laths and that the hollow tubes are formed by curling when the material is dispersed.

In the case of antigorite, which has a platy morphology, interest centers in the large *a* parameter (see below) which is considered to arise from a long period modulation of the simple layer structure, the precise nature of which has not been established, although various suggestions have been made (Aruja (1945); Onsager (1952); Zussman (1954)).

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* Contribution No. 55–63. College of Mineral Industries.

The term chrysotile has been widely used to describe fibrous serpentine, and the term antigorite for platy crystalline material. In addition, antigorite has often been applied to any non-fibrous serpentine. A more rigorous classification was suggested after a number of serpentine varieties had been studied by *x*-ray fibre and powder photographs (Whittaker and Zussman, 1956). This resulted in the recognition of a third variety, called lizardite (see Table 1). In addition a specimen from Unst (Brindley and von Knorring, 1954) and a synthetic Mg-Ge serpentine prepared by Roy and Roy (1954) appear to have a 6-layer orthocell. At this stage it will suffice to define the varieties of serpentine in terms of the data given in Table 1. Further discussion of nomenclature is given in a later section.

Table 1. Cell Parameters of Serpentine Minerals

	a, Å	*b*, Å	*c*, Å	β	Reference
1. Chrysotile (clino)	5.32	9.2	14.6	93°12′	Whittaker (1951)
Chrysotile (ortho)	5.32	9.2	14.6	90°	Whittaker (1953)
2. Antigorite	43.5	9.2	7.28	91°24′	Aruja (1945)
3. Lizardite	5.31	9.2	7.31	90°	Whittaker and Zussman (1956)
4. 6-layer ortho varieties:					
(material from Unst.)	5.32	9.22	43.6	90°	Brindley and von Knorring (1954); present text
(Synthetic Mg-Ge serpentine	5.44	9.42	44.7	90°	Present text

Because of the fine-grained nature of many serpentine varieties their characteristic morphology is unobservable in the light microscope, and structural information has been obtained only from *x*-ray powder patterns.

This paper describes the application of electron microscopy and electron diffraction to obtain further morphological and structural data on serpentine minerals. Dispersions were studied under the electron microscope to observe the morphology of different varieties and selected area diffraction patterns have been obtained from single crystals. These gave information about cell parameters and their relation to crystal morphology. It is not intended to discuss secondary morphological characteristics seen in the electron micrographs; the varieties of tubular form described by other workers have been observed, but the descriptions given here are limited to recognition of tubes, rolled sheets, laths, plates, etc.

DESCRIPTION OF SPECIMENS

Specimens were chosen for study so that each structural type previously observed was represented. Moreover, within a given structural group specimens showing marked differences in texture and/or appearance were selected. Wherever possible, specimens were chosen for which chemical analyses were available.

(*a*) *Clino- and ortho-chrysotiles*

1. *A silky fibrous chrysotile* (Transvaal). #M 14676, Manchester University, Dept. of Geology collection. Pale yellow silky fibre of a cross-fibre vein in massive serpentine occurring in dolomitic rock. *X*-ray fibre photograph shows a mixture of clino-chrysotile with approximately 15% orthochrysotile, the components within a bundle being very well aligned with the fibre axis, which is parallel to *a*. Evidence of complete disorder in direction of *b* axis. Photograph resembles a rotation pattern.

2. *A silky fibrous chrysotile* (Nunyerry, W. Australia) with high ortho-chrysotile content.

3. *A coarse splintery clino-chrysotile* (Findeten Glacier, Zermatt) #0.9652, Oxford University Museum collection; listed as "Schweizerite." Greenish yellow splintery fibres with greasy feel. *X*-ray powder photograph similar to that of (1). *X*-ray fibre photograph shows a moderate spread of fibre axis (*a*-axis) orientation.

(*b*) *Lizardites*

4. *Massive serpentine* (Snarum, Norway). #0.17788, Oxford University Museum. Light green, massive; no texture observable by *x*-ray methods. Powder pattern that of lizardite.

5. *Platy serpentine* (Lizard, Cornwall). Described by Midgley (1951). White soft flaky material. Single crystals give *x*-ray diffraction patterns showing misorientations of plates and some randomness in stacking of successive structural units. Powder photograph is that of lizardite.

6. *Bastite* (Baste, Harz, Germany). B.M. 170.

7. *Bastite* (Baste, Harz, Germany). B.M. 67807. Both bastites are from the British Museum collection. They are platy pseudomorphs after orthopyroxene and each gives the lizardite powder pattern.

(*c*) *Antigorites*

8. *Platy antigorite* (Antigorio, Italy). #0.16327, Oxford University Museum. Hard dark green platy specimen, crystals showing sweeping extinction between crossed nicols.

9. *Platy crystalline antigorite* (Glen Urquhart, Scotland) #C.76095, Department of Mineralogy and Petrology, Cambridge University (Harker Collection). Dark green specimen with platy parting, associated with some yellow fibrous material. Described by Francis (1956). Crystals are very small plates, showing patchy or sweeping extinction between crossed nicols and giving *x*-ray patterns which demonstrate their composite character.

10. *Platy crystalline antigorite* (Mikonui, New Zealand). #011566 (Harker Collection). Small rectangular plates in a fine grained green rock. X-ray data by Aruja (1945) (see Table 1, also Zussman (1954)).

11. *Platy crystalline antigorite* (Caracas, Venezuela). Described by Hess, Smith and Dengo (1952). Similar in texture, x-ray and optical properties to No. 10.

12. *Platy crystalline antigorite* (Antigorio, Italy). #C 70520 (Harker Collection). Similar to Nos. 10 and 11.

13. *Massive antigorite* (Yu Yen Stone, Manchuria) #94356, U. S. National Museum. White massive material showing patchy extinction between crossed nicols.

X-ray powder photographs of the last six specimens are closely similar but show some variations.

14. *Coarsely fibrous picrolite* (Shipton, Quebec). #T.W. 2914, Department of Mineralogy and Petrology, Cambridge University. Light green, brittle, lath-like splinters. X-ray fibre pattern shows b axis along fibre length, with moderate spread of orientation of fibre axis.

15. *Coarsely fibrous picrolite* (Harford Co., Maryland, U.S.A.) #481.83, Genth Collection, College of Mineral Industries, The Pennsylvania State University, U.S.A. Similar to specimen 14.

Powder photographs of 14 and 15 have fewer lines but these correspond approximately with the strongest lines of No. 10.

(*d*) *Other specimens*

16. *Synthetic Mg-Ge serpentine.* Prepared by Roy and Roy (1954). Very small but well developed single crystals, exhibiting platy habit with hexagonal outline.

17. *Massive serpentine* (Unst, Shetland Isles). Described by Brindley and von Knorring (1954). Olive green, massive resinous appearance. Powder pattern shows series of weak lines indicating long spacing; unique interpretation not possible from powder diagram.

18. *Coarsely fibrous serpentine* (Unst, Shetland Isles). Described by Brindley and von Knorring (1954). Aggregates of hard blue-green fibres. Fibre photograph shows orthochrysotile type of cell but with evidence of greater order in structure than occurs in specimen 1. Powder pattern similar to that from specimen 17 but lacks series of weak lines.

Electron Microscope and Diffraction Technique

Prior to obtaining electron diffraction patterns from the listed specimens each of them was prepared as a platinum shadowed disperson on a collodion substrate and examined in the electron microscope (R.C.A. model: E.M.U. type 2D) in order to determine the homogeneity of the sample and its predominant morphological features.

Freshly prepared unshadowed dispersions were then used to obtain electron diffraction patterns, and selected areas for diffraction were those containing wherever possible only one crystal, of a suitable size and thickness to give a good diffraction pattern. Sometimes it was not possible to achieve this ideal, and smaller crystals within the aperture area gave rise to superimposed but weaker patterns. Since prolonged exposure to the electron beam tends to weaken and broaden the diffraction spots, the pattern was photographed as quickly as possible, and immediately afterward an electron micrograph of the particular crystal was obtained. The instrument was such that its electron-optical system could be changed from microscopy to diffraction without disturbing the specimen.

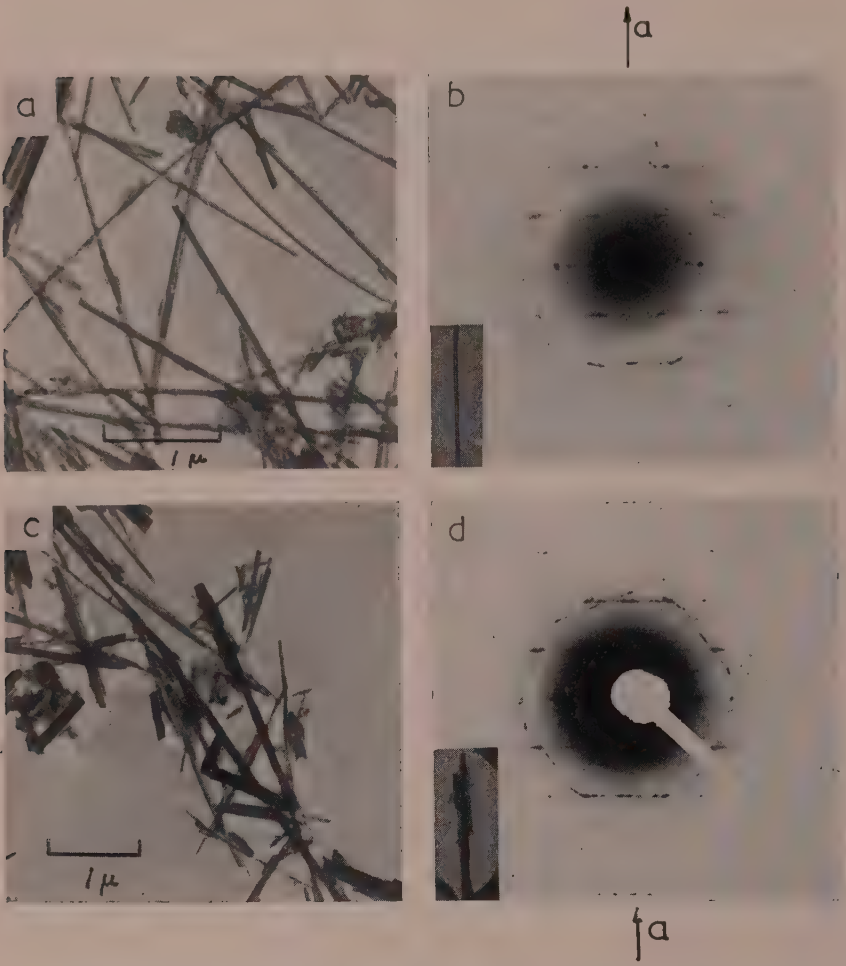
Unfortunately there was no means for tilting the specimen holder and consequently the patterns obtained were from crystals in orientations acquired in settling on the substrate. Thus for platy and lath-like particles the beam was always appproximately parallel to their shortest dimension, but could not be made accurately so.

Measurements of electron diffraction patterns recorded on plates were made on a magnified projected image, and then converted to give cell parameters by reference to diffraction patterns of MgO particles, which for each plate were produced with identical settings on the instrument's controls.

Description and Discussion of Micrographs and Diffraction Patterns

1. *Silky chrysotile* (Transvaal).

Electron micrographs (Fig. 1*a*) show elongated smooth-edged fibres frequently with a thin white axial line. One fibre and its electron diffraction pattern are shown in Fig. 1*b*. The diffraction patterns resemble closely those obtained by x-rays with the beam normal to a fibre bundle. Reflections are distributed along "layer lines," the spacing of which corresponds to the repeat distance $a = 5.32$ Å along the fibre axis. On the zero layer there occur $00l$ and $0k0$ spots, which implies a randomness of orientation about the fibre axis which could be given by a bundle of fibres or by a cylindrical lattice. On the first layer line are seen 110 and 130 bands and on the second $20l$ and $20\bar{l}$ spots. These reflections are in positions expected for the clino-chrysotile cell (see Fig. 2*e*) assuming rotation about the fibre axis. Similarly on the third layer there occur 310 and 330 bands and on the fourth $40l$ and $40\bar{l}$ spots. Such features have been described and discussed for the corresponding x-ray patterns by Whittaker (1954, 1955*a*, *b*) who states that the absence of hkl and $0kl$ reflections and the shapes and positions of $hk0$ bands indicate complete disorder with regard to the b axis and also point to the curved nature of the lattice. An x-ray diagram of a bundle of fibres which is a mixture of ortho- and clino-chrysotile does not indicate whether the different cells are confined to separate smaller fibres, or are more intimately intergrown, perhaps within a fundamental unit. Single elements of specimen



FIGS. 1*a* and *b*. Silky chrysotile: electron micrographs of dispersion and electron diffraction pattern from single fibre shown (Specimen No. 1).

FIGS. 1*c* and *d*. Splintery chrysotile: e.m. of dispersion and e.d. pattern from laths (Specimen No. 3).

(1) gave only the clino-chrysotile pattern, implying the separate existence of the two cell types.

2. *Silky chrysotile.*

The relation of ortho- to clino-chrysotile was tested more rigorously on a sample containing 60% ortho- and 40% clino-chrysotile. Some single fibres gave clino-chrysotile patterns (Fig. 2*b*) and others gave ortho-

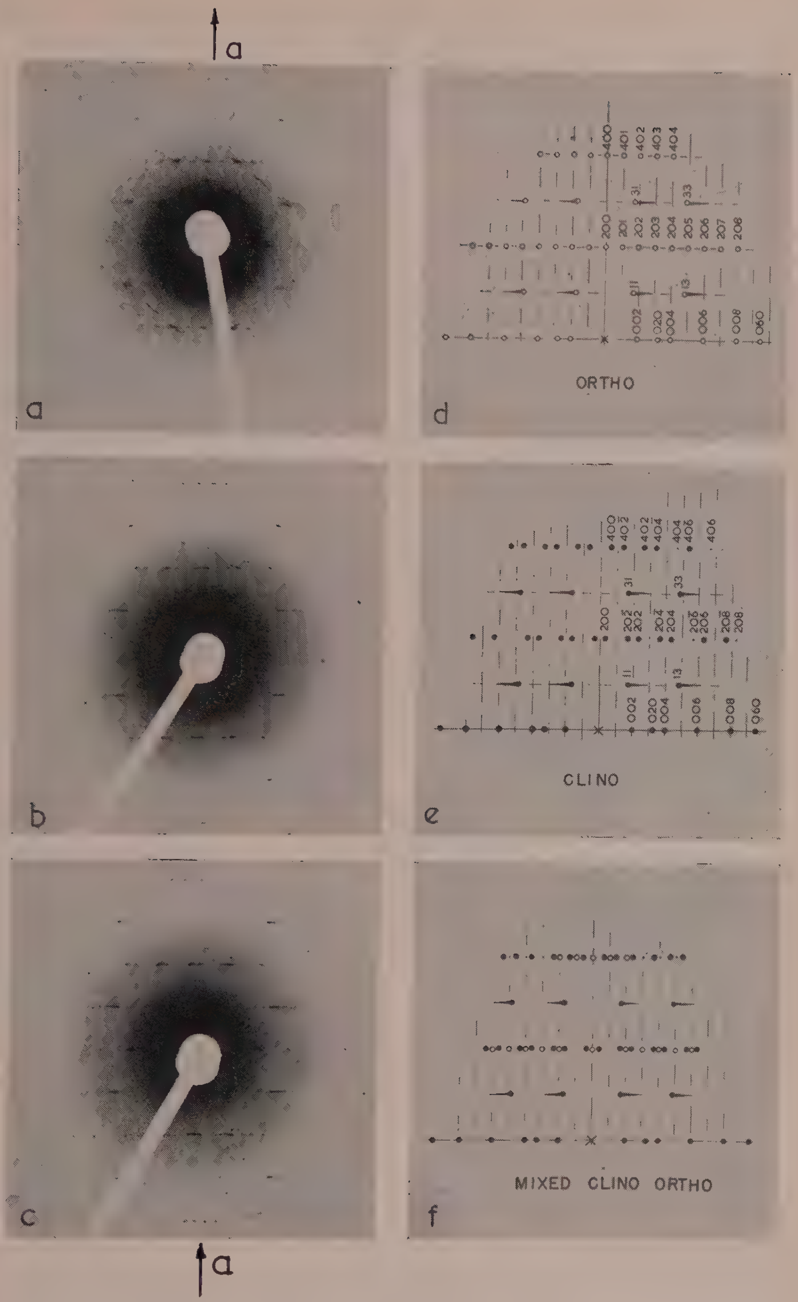


Fig. 2*a*. Ortho-chrysotile. e.d. pattern (Specimen No. 2).
Fig. 2*b*. Clino-chrysotile. e.d. pattern (Specimen No. 2).
Fig. 2*c*. Mixed ortho-, clino-. e.d. pattern (Specimen No. 9).
Figs. 2*d*, *e*, *f*. Idealized patterns for ortho-, clino-, and mixture respectively.

chrysotile patterns (Fig. 2*a*). Small sheaves of fibres seen in electron micrographs also gave patterns of either one type or the other, so that it may be concluded that in this case the mixture of cells is on a comparatively coarse scale.

Figs. 2*a*, *b* and *c* present typical electron diffraction patterns from ortho-chrysotile, clino-chrysotile, and a mixture of the two. Alongside of them, Figs. 2*d*, *e* and *f* are the corresponding idealized diagrams. These are mainly to illustrate the positions of possible reflections, no account being taken of relative intensities. For ortho-chrysotile, spots on even layers lie at intersections of an orthogonal network and are represented by open circles. Clino-diagrams are best viewed by reference to this network since $h0l$ and $h0\bar{l}$ spots (closed circles) are grouped in pairs about the intersections, as can be seen in Fig. 2*e*. Reflection positions at which no spots were observed are represented by small dots, and to avoid complication clino-chrysotile reflections with l odd are omitted from Fig. 2*e* even though a few weak ones actually occur. The original negatives must be carefully examined to see some of the weaker reflections indicated in Figs. 2*d*, *e*, *f*.

With other materials or under different conditions it is possible that either more or fewer reflections may be observed.

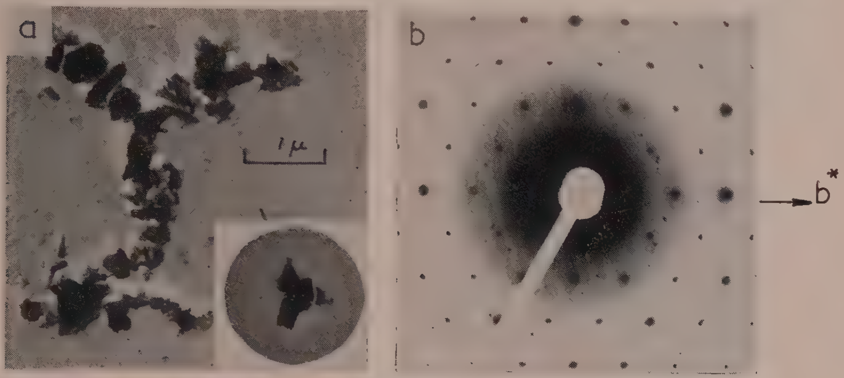
3. *Splintery clino-chrysotile* (Zermatt).

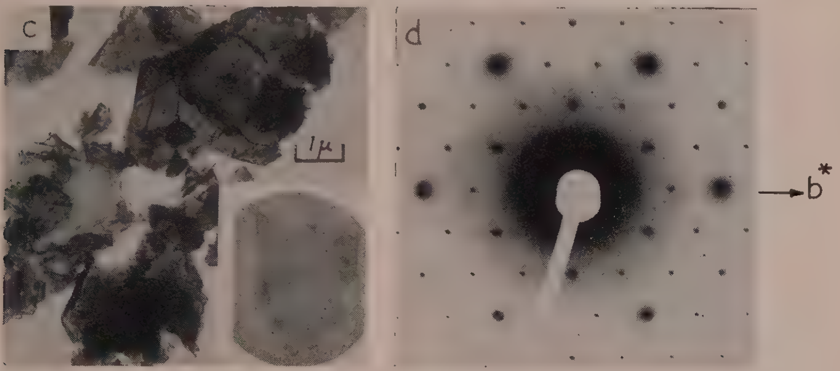
Although this was seen from its x-ray powder pattern to be purely clino-chrysotile it was included in the present investigation because of its markedly different macroscopic appearance. Electron micrographs (Fig. 1*c*) show mainly elongated laths of widths ranging up to about 2000 Å. Only relatively few thin particles show the white central line so that it may be inferred that the specimen is a mixture of laths with a small number of tubes.

Fig. 1*d* shows the electron micrograph of the selected area and the diffraction pattern obtained from it. Owing to the tendency of particles to cluster together it was difficult to select an area containing a single lath so that here, as in other photographs, more than one set of diffraction spots is seen. Reflections on the zero and even layers are very similar to those in the pattern of the silky fibres but include some $20l$ reflections with l odd corresponding to the 2-layer cell. On odd layer lines, however, the $hk0$ bands are fainter and several hkl spots (of the type $13l$) appear. These observations indicate less disorder in the stacking of successive layers which may be associated with a lath-like rather than tubular morphology. The presence of $0k0$ as well as $00l$ spots on the zero layer and several hkl's on odd layers implies that within a lath there are smaller units in various orientations about the lath axis.

4. *Massive serpentine* (Snarum, Norway).

Electron micrographs (Fig. 3*a*) show the irregular plate-like morphology of the fine particles. Since no single crystal or fibre patterns were obtainable by *x*-ray methods there has been no previous indication as to whether or not the lizardite unit cell is incorporated in a fine scale tubular structure. Furthermore this typical matrix material in which fibre veins are often found is often designated as antigorite. The fallacy of this is shown by *x*-ray powder photographs and it is even more apparent from the electron diffraction patterns. (Compare Fig. 3*b* with those of the antigorite group, Fig. 4*b* and *d*.)





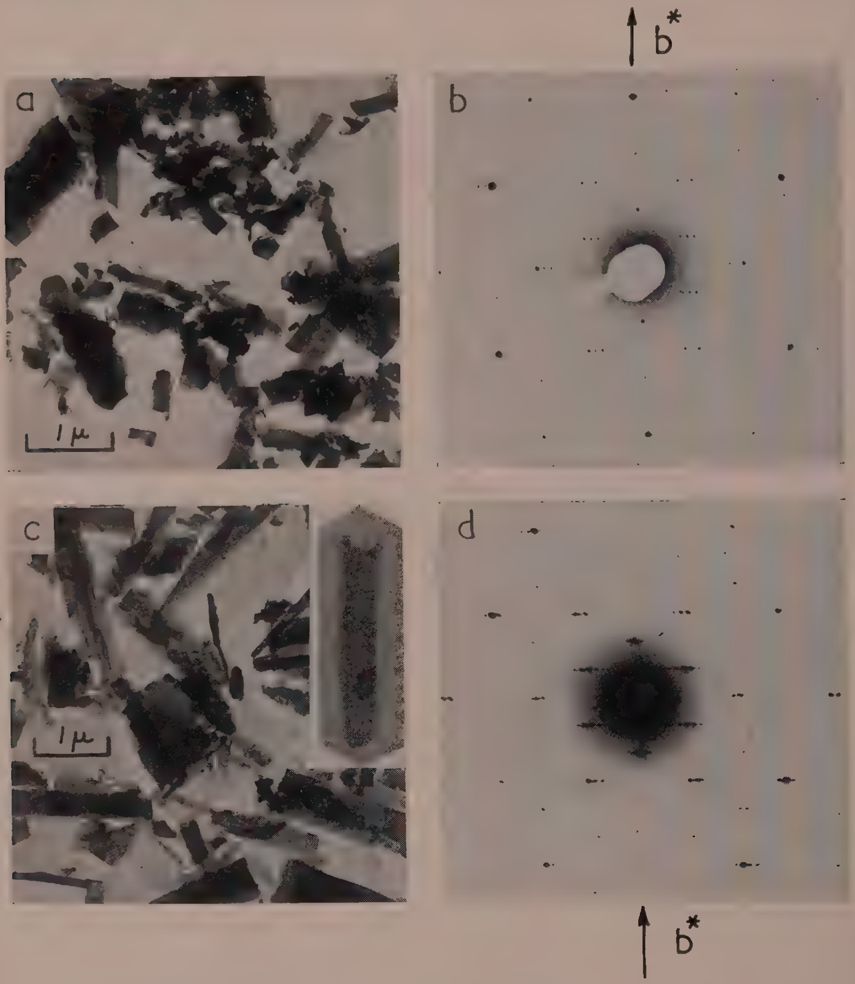
Figs. 3*a* and *b*. Lizardite (massive). e.m. of dispersion and e.d. pattern from crystal shown (Specimen No. 4).

Figs. 3*c* and *d*. Lizardite (platy). e.m. of dispersion and e.d. pattern from crystal shown (Specimen No. 5).

The pattern obtained from a single crystal of lizardite (Fig. 3*b*), is a hexagonal array of spots corresponding to a centered rectangular net of dimensions $a=5.2$ Å, $b=9.1$ Å in agreement with the *x*-ray powder pattern which gives $a=5.31$ Å, $b=9.20$ Å.

5. *White serpentine mineral* (Kennack Cove, Lizard, Cornwall).

This specimen, plate-like and flaky in hand specimen, gives electron micrographs (Fig. 3*c*) showing extensive thin plates, many with curled edges, and some small rod-like particles which may be rolled-up plates. The electron diffraction hexagonal array (Fig. 3*d*) yields the parameters a = 5.28 Å, *b* = 9.15 Å. These may be compared with values obtained by



FIGS. 4*a* and *b*. Antigorite (platy). e.m. of dispersion and e.d. pattern from single crystal (Specimen No. 8).

FIGS. 4*c* and *d*. Antigorite (fibrous). e.m. of dispersion and e.d. pattern from single crystal (Specimen No. 15).

the *x*-ray powder method, 5.31 and 9.20 Å, and from "single" crystal rotation photographs, 5.29 and 9.18 Å. Thus, although specimens (4) and (5) are so different in color and texture, both the *x*-ray powder patterns and the single crystal electron diffraction patterns show their structural similarity.

6. *Bastite* (Baste, Harz, Germany) B.M. 170.

7. *Bastite* (Baste, Harz, Germany) B.M. 67807.

X-ray powder patterns showed these to be lizardite and not antigorite.

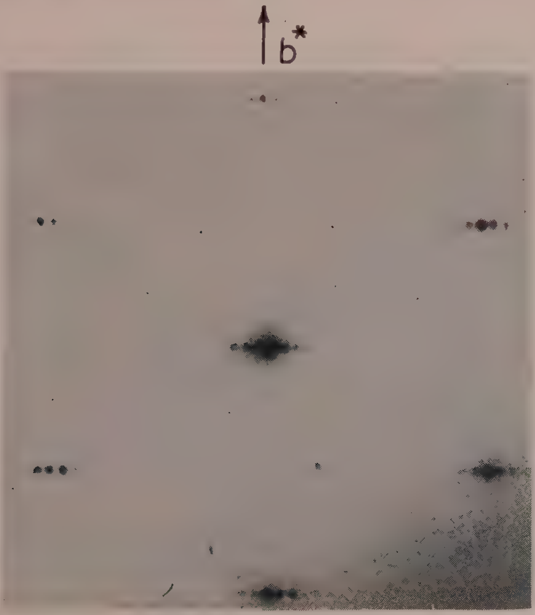


Fig. 5. Antigorite (massive). Part of e.d. pattern from single crystal of Yu Yén Stone, showing very closely spaced spots along a^* corresponding to $a \simeq 90$ Å. Scale 3× that of other diffraction patterns.

Electron micrographs and diffraction patterns confirm this and show the essential similarity between these and specimen No. 4.

8. *Antigorite* (Antigorio). Electron micrographs (Fig. 4*a*) show thin plates with approximately rectangular outline.

Electron diffraction patterns from single crystals are of the type shown in Fig. 4*b*. Layer lines are evident corresponding to a parameter $b = 9.30$ Å parallel to the longer morphological axis. Along each layer line, mainly grouped around reciprocal lattice points of a simple 5.3 Å

×9.2 Å rectangular net, are clusters of spots closely spaced at regular intervals corresponding to a cell parameter of approximately 38 Å. The pattern may be regarded as similar to those from plates of lizardite on which a superlattice periodicity along a^* has been superimposed.

9. *Antigorite* (Glen Urquhart, Scotland).

Electron micrographs of dispersions (Fig. 6) showed rectangular and irregular fragments accompanied in some cases by tube-like particles. This was difficult to understand in view of the plate-like nature of the gross material and it was later established that the fibrous particles came from an edge of the specimen which was yellow-brown and altered in appearance. Diffraction patterns of this tubular material identified it as clino-chrysotile. Some micrographs showed particles resembling wide tubes with wide bore or else elongated laths with curled edges. These too gave diffraction patterns of clino-chrysotile. A study of the fine structure in the $hk0$ bands appearing on patterns from single crysotile elements might reveal features characteristic of a particular curved formation (e.g., cylindrical, spiral, helical (Whittaker 1955*c*)). One pattern showed spots of both clino- and ortho-chrysotile (Fig. 2*c*) but the selected area contained more than one particle.

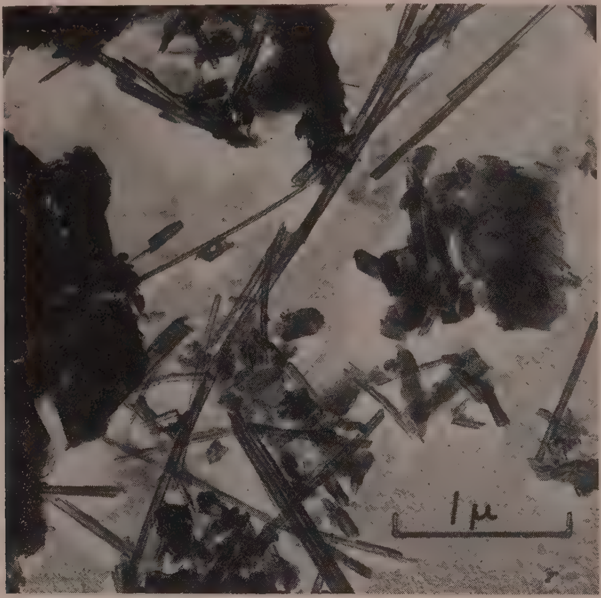


FIG. 6. Antigorite and chrysotile. e.m. of mixture (Specimen No. 9).

The plates of antigorite gave patterns similar to that shown in Fig. 4*b* yielding in most cases the values $b = 9.30$ Å, $a = 38$ Å, but some crystals gave $a = 34$ Å.

In order to investigate further the apparently variable *a* parameter of antigorite many more crystals from different specimens were examined and an analysis of these results is presented later.

10. *Antigorite* (Mikonui, New Zealand).

Patterns of the type shown in Figs. 4*b* and *d* were obtained from elongated, roughly rectangular platy crystals. Layer line spacing gave $b = 9.32$ Å (*b* parallel to crystal length), and the superlattice parameter was determined as $a = 43.1$ Å (c.f. *x*-ray single crystal measurements).

11 and 12. *Antigorites* (Caracas and Antigorio). These appeared in electron micrographs to have morphology similar to that of 10 and gave similar electron diffraction patterns exhibiting a variety of superlattice parameter values.

13. *Antigorite* (Yu Yen Stone). This very fine grained white material appeared in electron micrographs as irregular plate-like fragments sometimes showing a vaguely hexagonal outline. Many diffraction patterns (Fig. 5) show very closely spaced spots and yield parameters $a = 90$ Å to 110 Å, $b = 9.2$ Å; some yielded $a \simeq 41$ Å.

14. *Picrolite* (Shipton, Quebec).

Micrographs show plates and laths, but also some tubular material giving the diffraction pattern of clino-chrysotile. Diffraction from the plates yielded patterns similar to Fig. 4*d*.

15. *Picrolite* (Maryland, U.S.A.)

Electron micrographs show plates and broad laths (Fig. 4*c*), and the single crystal pictured gave the diffraction pattern in Fig. 4*d* ($b = 9.26$ Å, $a = 35.4$ Å).

16. *Synthetic (Mg-Ge) serpentine.*

Electron micrographs (Fig. 7*a*) show fairly thick plate-like crystals, some displaylng sharp edges with a hexagonal outline. The diffraction pattern (Fig. 7*b*), comes from the thin crystals shown in the inset and resembles that of lizardite in being a hexagonal network. This yields the parameters $a = 5.40$ Å, $b = 9.40$ Å, which are larger than those of the Mg-Si serpentines.

The *x*-ray powder pattern from this synthetic serpentine contained very many closely spaced sharp lines indicating a large unit cell and a well ordered crystal structure. The lines were all indexed using cell dimensions $a=5.43_5$ Å, $b=9.41_5$ Å, $c=44.66=6\times 7.44_5$ Å, $\beta=90°$.

An $02l$ series of lines following closely on 020 (or 110) recalls the series which was reported for the specimen from Unst. In that case, Brindley and von Knorring (1954) suggested two possible explanations, namely that they could be indexed as $H20$ or as $02L$ lines corresponding to superlattices $a=43.6$ Å or $c=3\times 14.53$. These proposals have been further discussed by Zussman (1956). For the Mg-Ge serpentine, confirmation that the large parameter 44.66 Å is not associated with the a axis is provided by the electron diffraction pattern (Fig. 7*b*) since, unlike antigorites, it has no closely spaced spots in the a^* direction. It seems likely therefore that specimens 16 and 17 both contain a 6-layer cell.

17. *Massive Serpentine* (Unst, Shetlands).

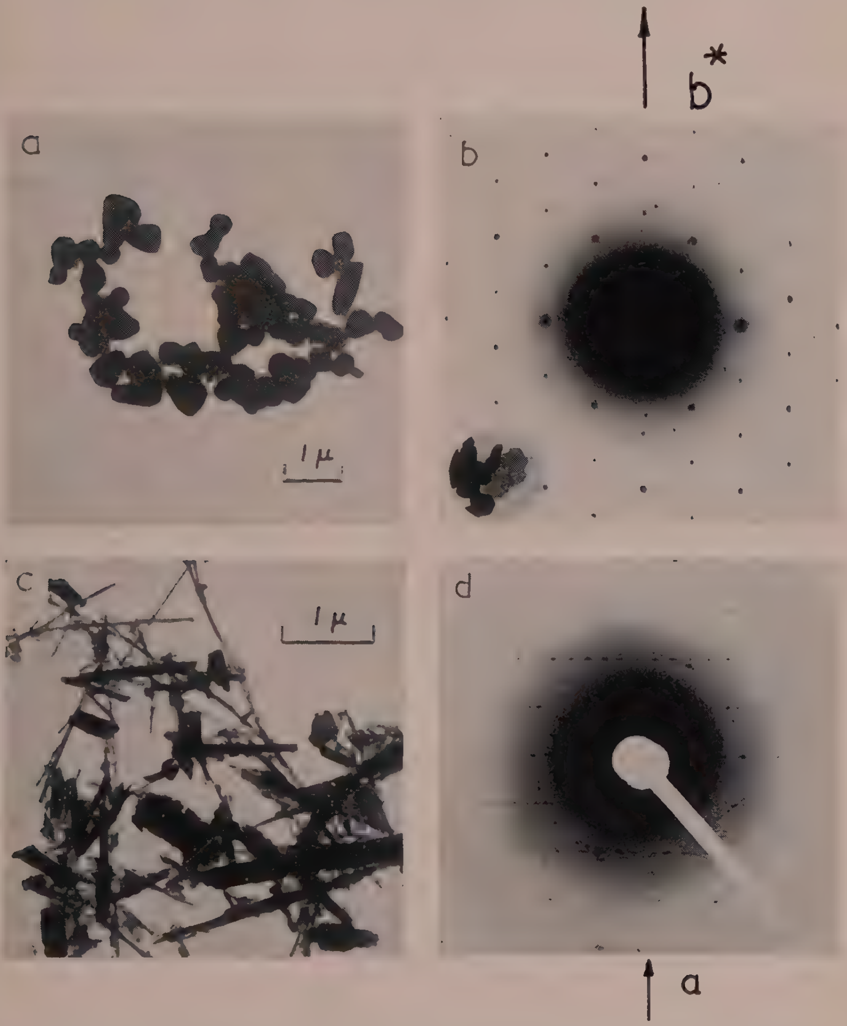
Particles of this material are seen to be predominantly lath-like (Fig. 7*c*), and their electron diffraction patterns (Fig. 7*d*) differ from any of those previously described. Layer lines indicate a repeat distance along the lath axis, $a=5.35$ Å $\pm 1\%$, and there is no indication of a long parameter in this direction. On the zero layer are seen $00l$ and $0k0$ reflections and in some cases weak $0kl$ spots. On even layers $h0l$'s occur corresponding to a cell with $c=14.5$ Å, including some strong reflections when l is odd and also some weak $hk0$ and hkl spots. On odd layers, $hk0$ and hkl spots appear which are consistent with a cell, $a=5.35$, $b=9.3$, $c=14.5$ Å, $\beta=90°$. Thus the pattern is one which may be derived by the rotation about a of a cell similar to that given for ortho-chrysotile by Whittaker (1951), and is compatible with the main reflections on the x-ray powder photograph presented by Brindley and von Knorring. However a few additional weak spots are sometimes observable on the first layer line which may correspond with some of the series of weak reflections following 020 in the x-ray powder pattern. To summarize this discussion, the new evidence points clearly against this material having the antigorite type cell, but provides only weak additional evidence for the 6-layer cell.

18. *Fibrous serpentine* (Unst, Shetlands).

Electron micrographs show slender lath-like fragments which give diffraction patterns similar to that shown in Fig. 7*d*.

ANALYSIS OF DATA FROM SINGLE CRYSTAL PATTERNS

The clusters of spots observed in electron diffraction patterns of antigorites are similar to those obtained by x-ray diffraction from single crystals of antigorite from Mikonui (Aruja 1945, Zussman 1954), and may be similarly interpreted as evidence of a large superlattice cell. However, the clusters also recall the unusual effects observed by other workers, e.g. from mica (Darbyshire and Cooper 1935), from ZnO (Rees and Spink 1950), from molybdenite (Finch and Wilman 1937, Uyeda, Ichinokawa and Fukano, 1954). In the case of mica, clusters of spots



FIGS. 7*a* and *b*. 6-layer ortho-serpentine (synthetic Mg-Ge): e.m. of dispersion and e.d. pattern from crystals shown (Specimen No. 16).

FIGS. 7*c* and *d*. 6-layer ortho-serpentine (Unst): e.m. of dispersion and e.d. pattern from single lath (Specimen No. 17).

were attributed to *hkl* reflections occurring alongside of *hk*0's through bending or rotation of the crystal. In the case of ZnO and molybdenite, very close subsidiary maxima occur which are attributed to the limitation of crystal size. With these and other similar explanations in mind, the patterns of antigorite have been carefully examined, and it has been concluded that they are not explicable in such terms. They are entirely consistent with a structure involving a large *a* parameter which repeats with great regularity in successive cells of any given crystal.

Table 2. Antigorites: *a* Parameter Measurements, in Å Units

Antigorio (O. 16327)	Antigorio (C. 70520)	Glen Urquhart	Mikonui	Caracas	Shipton, Quebec (Picrolite)	Harford Co., Md. (Picrolite)	Yu Yen Stone	Average
		33.4						
		33.5						
		33.9						33.7
		33.9						
		34.0						
						35.1		
						35.1		
						35.4		
						35.6		35.5
						35.7		
	36.2					36.2		
						36.4		
37.6	38.1	37.9						
38.7	38.6	38.0						
38.9	38.6	38.0						
	38.8	38.1						38.3
		38.1						
		39.0						
41.1	40.6		41.1	41.1	40.5			
			41.4	41.4	41.4	41.1		41.1
			41.7			41.5		
	42.3		42.7	42.4				
	42.6		43.1	42.4				
	43.0		43.5	42.8				43.1
			43.7	43.2	43.9			
			44.0	43.6				
							88.6	
							90.6	90.6
							92.6	
							108	109
							110	

In view of the variation from one pattern to another of the distances between the closely spaced spots in antigorite patterns, a study has been made of the sources of error involved, and the significance of the results has been evaluated.

Parameters derived from electron diffraction spot patterns are subject to errors introduced by the method of calibration and measurement, and possibly also by missetting of the crystal. Thin platy crystals can give a complete array of spots even when they are not exactly perpendicular to the beam, since reciprocal lattice points are in this case extended into "rods" in reciprocal space. If the $a \cdot b$ net plane is tilted about b by an angle ϕ, measurement of the spot pattern will give parameters b and $a \cos \phi$. Thus when control of crystal orientation is not possible, low values of the parameters may be obtained, the effect being most marked for distances measured normal to the axis of tilting. In the cases of the Mg-Ge serpentine and the lizardites, which produce hexagonal arrays of single spots, tilting can be detected by non-equivalence of spacings measured in symmetrically related directions; in some cases a tilted crystal can distort a rectangular spot pattern into an oblique one.

In most cases described here, crystals tended to lie with the principal net plane perpendicular to the beam, but orientation could not be further controlled. However, a crystal grossly tilted about b could be recognized by its effect on the average distance between clusters, and such patterns were disregarded.

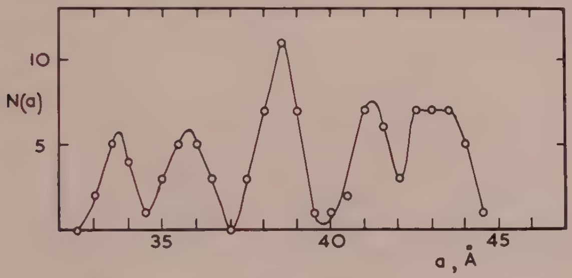


FIG. 8. Distribution of a parameter values among antigorites.

Measurements of MgO powder rings indicated that a standard deviation of 1% in parameter value due to calibration and measurement errors could be expected. The mean value of the b parameter from a large number of determinations with a standard deviation of 1.1%, was 9.26 Å, indicating that there is little or no tilting affecting these measurements, and that b is more or less constant for all antigorites.

The values of a for antigorites were measured on many different patterns and are seen to fall into groups such that with one exception no member of a group differs by more than 2% from the mean (Table 2). It is certain that the differences in values recorded cannot be explained by crystal tilt, and that they are far greater than the estimated limits of experimental error. Table 2 also shows that not all possible values of a

are actually adopted in antigorite crystals but that certain values are "preferred." This is further illustrated in Fig. 8 where N(a), the number of specimens with parameter $a \pm 0.5$ Å, is plotted against a, and peaks occur centered on 33.7, 35.8, 38.6, 41.2 and 43.0 Å. However, the difficulty of allowing for the fact that some crystals may give slightly low values through tilting makes it unwise to attach a too precise significance to the exact numbers quoted.*

Discussion and Conclusions

Electron microscope and electron diffraction studies have been used to examine the morphology, the unit cell parameters, and their interrelations in the serpentine minerals. They have been particularly useful where crystallite size has been too small for x-ray single crystal techniques, and have supplemented and sometimes modified previous concepts based on x-ray powder patterns alone. The main conclusions drawn from the presented results are summarized under appropriate headings below.

Chrysotile

Crysotile occurs in either silky or splintery fibres which in the dispersed state appear in electron micrographs as tubes and laths respectively. Electron diffraction patterns from single units of the silky variety still bear the features of a "rotation" pattern; they must therefore either contain smaller randomly oriented filaments, or else possess some tubular or roll-like configuration. Diffraction patterns from laths are also of the rotation type but indicate a greater degree of order in the fundamental crystallites.

Bundles of silky fibres were seen by x-ray diffraction to contain both ortho- and clino-chrysotile, but single elements of these gave electron diffraction patterns of either one cell or the other. Thus, it appears that ortho- and clino-chrysotile exist in separate strands.

Lizardite

The two specimens, #4 and #5, which are apparently very different, #4 being green and massive, #5 white and platy, are found to be fundamentally similar in that #4 is also platy on a fine scale, and both give similar x-ray and electron diffraction diagrams. The latter show hexagonal arrays of spots corresponding to the $a \cdot b$ net plane which lies in the plate and is perpendicular to the electron beam.

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* Not shown in Fig. 8 are values obtained from specimen 13 (Yu Yen Stone). Its patterns yield a parameters 41 Å, 90 Å and 110 Å. Furthermore, one specimen of a fibrous antigorite examined by J. A. Gard of Aberdeen University, yielded $a = 18.6$ Å.

Two bastites examined have similar morphology and give diffraction patterns similar to those of other lizardites.

Antigorites

Antigorites and picrolites were grouped together on the basis of *x*-ray powder patterns although the latter are fibrous, and it was thought (Whittaker and Zussman, 1956 (pt. 2)) that all possessed the same large cell with $a=43.5$ Å. The present work shows that single picrolite crystals are lath-like and give electron diffraction patterns of the antigorite type. These patterns may be approximately described as those of an $a \cdot b$ net plane, with b parallel to the longer axis of the crystal, but with closely spaced spots of a superlattice in the a direction superimposed.

The superlattice parameter a is not constant, but takes a number of different values even among crystals from one specimen, and there are indications that certain values of a are preferred.

6-layer ortho-serpentines

A synthetic Mg-Ge serpentine has been allocated a six layered ($c=6\times 7.44_5$ Å) unit cell in order to index the many lines of its *x*-ray powder pattern (unpublished data). Confirmation that its large 44.7 Å axis is not of the antigorite type was provided by electron diffraction.

Micrographs of serpentine specimens from Unst, Shetlands, show laths which give spot patterns largely compatible with rotation of a 2-layered ortho-cell about the lath axis ($a=5.3$ Å) but also showing faint indications of a 6-layer cell. This evidence, together with the absence of antigorite characteristics, and the previous *x*-ray evidence, all support the view that this material is structurally similar to the 6-layer Mg-Ge serpentine.

NOMENCLATURE

In the light of the present studies some comment may be made concerning the naming of serpentine minerals. The classification presented by Whittaker and Zussman (1956) needs to be modified in some respects. As regards antigorite it was stated that only those specimens should be so called which give the *x*-ray powder pattern obtained from the variety from Mikonui. At that time this was the only variety from which single crystal *x*-ray patterns had been obtained. The principal features of the antigorite pattern are indeed shown by all of them but differences were noted which can now be attributed to the range of values adopted by the large a parameter. It seems reasonable that, for the present at least, the name antigorite should be applied to all serpentines possessing the large a parameter. Picrolites appear to be essentially antigorites with a splintery fibrous character and therefore would be better termed "fibrous antigorite."

For the massive and columnar serpentine from Unst, Shetlands, it seems that their large parameter is $c=6\times 7.265=43.59$ Å and not the a parameter. Therefore, the name "ortho-antigorite" (Brindley and v. Knorring 1954) is no longer apposite. Such varieties can conveniently be called "6-layer ortho-serpentines."

The serpentine classification can now be represented as in Table 3. The table also indicates broadly the morphology (of each group) as seen in hand specimen and when dispersed in the electron microscope.

It is still premature to attempt to describe serpentine varieties with a systematic notation conveying symmetry and number of layers per cell such as Levinson (1955) has developed for the micas because many details of the serpentine structures have yet to be evaluated.

Table 3. Serpentine Classification

	Serpentines					
	Chrysotile	Lizardite	6-Layer Serpentine		Antigorite	
	Clino, Ortho, Para*				(various a parameters)	
Morphology (hand specimen)	fibrous; occasionally massive	massive or platy	massive, fibrous	platy	massive, platy	fibrous
Morphology (dispersed state, electron microscope)	tubes, laths	plates	laths	plates	plates	broad laths

* Para-chrysotile a component of silky fibre bundles was mentioned briefly by Whittaker and Zussman (1956) and its structure is to be further discussed by Whittaker in a future paper.

In conclusion it is suggested that the terms "antigorite" and "chrysotile" should not be used loosely as being synonymous with "massive" and "fibrous." The four principal varieties can usually be identified by they x-ray powder patterns, but a more detailed designation can be achieved by careful examination of single crystal or fibre patterns obtained by x-ray and/or electron diffraction methods supplemented by electron micrographs.

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DISCORDANT U-PB AGES AND MINERAL TYPE*

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Abstract

The discordant ages obtained from the isotopic ratios Pb^{206}/U^{238}, Pb^{207}/U^{235}, Pb^{207}/Pb^{206} and Pb^{208}/U^{232} in various minerals are considered in terms of the mineral type. The available pertinent data including some new measurements made at this laboratory are compared. Each mineral structure appears to show a consistent but characteristic discordance, except monazite, which exhibits a dual behavior; i.e., pitchblende $206/238 < 207/235 <$ probable age; uraninite $208/232 < 206/238 < 207/235 <$ probable age; monazite, xenotime $208/232 <$ probable age $< 207/235 < 206/238$; monazite $208/232 < 206/238 < 207/235 <$ probable age; zircon and sphene $208/232 \ll 206/238 < 207/235 <$ probable age; samarskite, thorite, sphene $208/232 < 206/238 < 207/235 <$ probable age; euxenite $206/238 < 207/235 < 208/232 =$ probable age. On the other hand if adequately preserved, concordant ages can be obtained from almost any radioactive mineral. Mineral structures differ considerably in their stability to alteration. For a given mineral the isotopes of lead derived from uranium decay must be in a different lattice environment than the Pb^{208} derived from thorium decay.

Introduction

The lack of agreement among the ages derived from the isotopic ratios of uranium, thorium and lead is one of the most important problems in geochronometry. Nier (1939) pointed out the problem in discussing his first isotopic ages by the uranium-lead method. Later, Holmes (1948) attempted to explain the most common age discordance of $Pb^{206}/U^{238} < Pb^{207}/Pb^{206}$ as a result of radon leakage, but Giletti and Kulp (1954) measured a representative suite of uranium minerals and found that the radon leakage for fresh primary minerals seldom exceeded a few per cent although in the case of very fine pitchblende, the value could reach 10% and some secondary minerals such as carnotite could reach 20–30%. If these data are combined with the observation of G. Tilton (personal communication) that the leakage under laboratory conditions will be maximal, it is concluded that radon leakage is not very important. For post-Cambrian minerals, however, the 207/206 age is quite sensitive to radon leakage.

Eckelmann and Kulp (1956) made a detailed study of the Lake Athabasca district pitchblendes. The ages within a specific sample as well as the ages from sample to sample showed major discordance. It was concluded that the dominant factor causing this discordance was lead loss and that the lead removal was most probably due to temperature rises at certain periods during the history of the mineral. This same pattern of ages appears at the Sunshine Mine, Idaho, and in the Witwatersrand pitchblende and thucolite deposits but is not evident at Katanga, Belgian Congo.

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Stieff et al. (1953) have suggested that the deposition of old radiogenic lead along with the pitchblende can also explain the observed discordance and they cite evidence for this in the Colorado Plateau ores. Such a phenomenon could produce the observed isotopic ratios but would require the same hydrothermal solution which transported the uranium to also carry old radiogenic lead with essentially no contamination from common lead, and that deposition of the uranium and lead took place at the identical spots. It would be easiest for such a process to produce erroneous isotopic ratios in very young ores such as occur in the Colorado Plateau. Nevertheless if this were the case it would be expected that a representative sampling of intimately associated galena would show a preponderance of old radiogenic lead. Since this is not the case and since the observed pattern of ages is very slightly affected even if the most radiogenic lead is used for the corrections, the hypothesis of old radiogenic lead addition remains to be demonstrated. Certainly this process would not appear to be of any significance in pegmatite minerals.

Earlier some of the discordance of the ages was attributed to uncertainties in certain of the physical constants, particularly the half-lives of Th^{232} and U^{235}. The agreement in all of the isotopic ages for a few older samples (e.g. Bikita at 2650 m.y.) and the great variation in the degree of discordance observed with different minerals eliminate this as a significant source of error. Both the U^{235} and Th^{232} half-lives appear to be correct to at least 2%. Analytical error in the wet chemical method for lead can account for some cases of discordance in the analysis of lead in young minerals where the lead concentration is only a few tenths of a per cent. Here the apparent reproducibility is ±5% but the real value can be off by as much as 20% in some cases. This problem can be eliminated by using isotope dilution techniques.

Tilton (1956), who has conducted leaching experiments with dilute HCl on powdered samples for which the isotopic ages had been obtained, has examined the isotopic composition of the leach. He was able to show (1) in general, there is a correlation between the isotopic composition of the lead removed by dilute acid treatment and the observed age pattern obtained from the bulk sample (Tory Hill, Ont.). Thus in a zircon for which the Pb^{208}/U^{232} age is much lower than the Pb^{206}/U^{238}, the Pb^{208} is leached out more easily than Pb^{206} and Pb^{207}. (2) Thorium and uranium are removed in the leaching process as well as lead. In those samples where $206/238 > 207/206$, uranium is leached preferentially to lead where the $Pb^{208}/Th^{232} < Pb207/206$, Pb^{208} is leached preferentially to the other lead isotopes as well as to the thorium. (3) In the case of the samples that were analyzed, it was demonstrated that the readily leachable material was not added from outside since adjacent minerals give a totally different leach composition that is consistent with their own bulk composition. (4) The loss of lead isotopes during the history of a mineral is not necessarily proportional to the present abundance. Tilton's study did not represent the condition under which alteration of radioactive minerals actually takes place but clearly demonstrated that the readily mobile constituents in a given mineral structure are related to the age abundance. Ahrens (1955) has suggested that the high 206/238 ages for the Huron Claim and Las Vegas monazites are due to the error in the uranium analyses. It is not likely that this is the case, however, since the Carnegie Institute Annual Report 1954–1955 reports an identical pattern on analyzing monazite samples by the isotope dilution technique.

Discordance and Mineral Type

Enough data have now accumulated to warrant a preliminary analysis of the effect of mineral structure on the discordance of the ages. It appears from the foregoing discussion that loss of uranium, thorium and lead can take place under varying conditions. In a strongly acid environment such as might occur in the surface weathering of a pitchblende-sulfide complex, Phair and Levine (1952) have shown that uranium is leached preferentially to lead, but this situation is not a common one in nature. Føyn (1938) has reported an experiment in which lead exsolved from uraninite at elevated temperature (∼300°) and pressure in a bomb with only water added.

The present isotopic composition in any sample, therefore, is dependent on the pressure, temperature and chemical environment to which a particular mineral lattice has been subjected at different periods in its history as well as the initial crystal structure.

Representative isotopic ages are compiled in Table 1 according to mineral type. The following conclusions can be derived from these data:

(1) Apparently all minerals can give concordant ages, i.e., Katanga pitchblende; Romteland, Norway and Nicolls Nob, Australia uraninites; Bikita, South Rhodesia and Goodhouse, South Africa monazites; Ceylon zircon and Marievale and Blijvoorvitzicht, South Africa thucolites. (It is interesting to note that the South African thucolites give concordant ages but apparently do not represent the true age of initial uranium mineralization. This is probably a case of "accidental concordance" described by Wetherill (1956).)

Examples of other minerals with concordant ages could doubtless be found if enough samples were analyzed. This observation shows that the

TABLE 1. ISOTOPIC AGES FROM VARIOUS URANIUM AND THORIUM MINERALS
(Age in m.y.)

A. *Pitchblende*

Locality	206/238	207/235	207/206	210/206	Reference
Colorado Front Range					
Wood Mine	55 ± 1	56 ± 2	150 ± 110	—	Nier et al. (1941).
Richards Mine	56 ± 1	62 ± 6	320 ± 230	—	Eckelmann & Kulp (1957).
German Mine	51 ± 1	54 ± 2	315 ± 100	—	Eckelmann & Kulp (1957).
Sunshine Mine	805 ± 10	860 ± 20	1035 ± 35	—	Eckelmann & Kulp (1957).
Great Bear Lake					
Eldorado Mine	1230 ± 10	1305 ± 15	1405 ± 45	1230 ± 40	Eckelmann & Kulp (1957).
Eldorado Mine	1010 ± 5	1100 ± 10	1240 ± 20	1040 ± 40	Eckelmann & Kulp (1957).
Eldorado Mine	1220 ± 10	1275 ± 15	1395 ± 20	—	Nier (1939).
Saskatchewan-Manitoba (Lake Athabasca District)					
ABC Adit	335 ± 15	395 ± 15	730 ± 30	355 ± 8	Eckelmann & Kulp (1956).
Eagle Mine	895 ± 5	975 ± 10	1140 ± 30	890 ± 25	Eckelmann & Kulp (1956).
Ace Mine	1280 ± 10	1490 ± 10	1780 ± 20	1280 ± 30	Eckelmann & Kulp (1956).
Ace Mine	1550 ± 10	1630 ± 10	1795 ± 15	1535 ± 45	Eckelmann & Kulp (1956).
Belgian Congo, Africa					
Katanga	575 ± 5	595 ± 5	630 ± 40	—	Eckelmann & Kulp (1956).
Katanga	616	614	610	—	Nier (1939).
Czechoslovakia					
Joachimsthal	178 ± 2	195 ± 10	385 ± 135	—	Lamont (unpublished)
South Africa					
Witwatersrand	1386	1610	2070	—	Lamont (unpublished)

B. *Uraninite*

Locality	206/238	207/235	207/206	208/232	Reference
Huron Claim S.E. Manitoba	1564	1985	2475	1273	Nier (1939).
Huron Claim S.E. Manitoba	1860	2170	2505	1360	Eckelmann & Kulp (1957).
Viking Lake Manitoba	1850	1880	1920	1670	Wasserburg & Hayden (1955).
Viking Lake Manitoba	1525	1720	1870	445	Eckelmann & Kulp (1957).
Lac La Ronge Manitoba	565	868	1750	—	Eckelmann & Kulp (1957).
Black Hills South Dakota	1580	1600	1630	1440	Tilton et al. (1956).
Black Hills South Dakota	1615	1615	1622	1370	Eckelmann & Kulp (1957).
Black Hills South Dakota	1390	1460	1610	1030	Eckelmann & Kulp (1957).
Wilberforce	1077	1050	1035	983	Nier (1939).
Wilberforce	1015	1038	1060	—	Eckelmann & Kulp (1957).
Wilberforce	1000	1015	1030	1010	Nier (1941).
Wilberforce	1000	1020	1085	870	Wasserberg & Hayden (1944).
Wilberforce	994	993	982	897	Wasserberg & Hayden (1955).
Romteland Norway	890	892	920	900	Lamont (unpublished).
Nicoll's Nob Australia	445 ± 5	430 ± 15	340 ± 75	435 ± 15	Lamont (unpublished).

TABLE 1—*Continued*

Locality and Mineral	206/238	207/235	207/206	208/232	Reference
			C. *Monazite*		
Ebonite Claims So. Rhodesia	2640	2670	2700	2640	Holmes (1954)
Jack Tin Claims So. Rhodesia	2210	2460	2660	1940	Holmes (1954)
Irumi Hills No. Rhodesia	1990	2330	2640	1380	Holmes (1954)
Huron Claim Manitoba	3220	2840	2590	1830	Nier (1939)
Antsirabe Madagascar	1370	1850	2450	610	Holmes and Cohen (1955)
Yadiur India	1410	1820	2330	1800	Holmes (1955)
Ene India	4300	3100	1600	540	Holmes (1955)
Las Vegas New Mexico	1730	1560	1340	770	Nier et al. (1941)
Quartz Creek Colorado	1590	1420	1170	995	Tilton (1956)
Mount Isa Australia	—	—	1160	1000	Nier et al. (1941)
Steenkampskraal So. Africa	1080	—	—	990	Tilton and Nicolaysen (1957)
Soniana India	635	700	910	610	Holmes et al. (1949)
Houtenbeck So. Africa	1400	1230	930	940	Tilton (1956)
Goodhouse So. Africa	930	915	880	900	Tilton (1956)
			D. *Zircon*		
Quartz Creek Colo.	930	1130	1540	515	Carnegie Re. 1954–1955.
Tory Hill, Ont. (−200 mesh)	1030	1055	1090	390	Carnegie Re. 1954–1955.
Tory Hill, Ont. (1–2 mm)	940	960	1015	—	Carnegie Re. 1954–1955.
Bagdad, Ariz. (−200 mesh)	630	770	1210	270	Carnegie Re. 1954–1955.
Natural Bridge, N.Y. (2–3 cm)	1025	1065	1140	—	Carnegie Re. 1954–1955.
Ceylon (2–3 cm)	540	544	555	538	Carnegie Re. 1954–1955.
Cape Granite South Africa	330	355	525	237	Carnegie Re. 1954–1955.
			E. *Samarskite*		
Petaca District New Mexico	240	310	875	180	Eckelmann & Kulp (1957).
Spruce Pine North Carolina	282	292	405	170	Eckelmann & Kulp (1957)
Spruce Pine North Carolina	307	312	380	205	Eckelmann & Kulp (1957).
Spruce Pine North Carolina	314	316	342	302	Eckelmann & Kulp (1957).
			F. *Euxenite*		
Romteland Norway	485	560	910	920	Lamont (unpublished).
Kalstad Norway	450	530	940	980	Lamont (unpublished).

TABLE 1—*Continued*

Locality	206/238	207/235	207/206	208/232	Reference
			G. *Microlite*		
Harding Mine New Mexico	916	996	1180	—	Carnegie Inst. Re. 1954–1955.
Quartz Creek Colorado	915	1055	1350	—	Tilton (1956).
			H. *Others*		
Romteland, Norway (Thorite)	740	760	830	594	Lamont (unpublished).
Swaziland, Africa (Yttrotantalite)	1105	1455	2060	1270	Lamont (unpublished).
Quartz Creek, Colo. (Columbite-tantalite)	1520	1470	1390	—	Tilton (1956).
Uncompahgre, Colo. (Biotite-xenotime)	3180	2065	1640	1100	Tilton (1956).
Tory Hill, Ont. (Sphene)	910	—	—	—	Tilton (1956).
Tory Hill, Ont. (Sphene)	—	—	1090	450	Tilton (1956).
Besner, Ont. (Thucolite)	262	275	440	250	Nier (1939).
Witwatersrand (Thucolite)					
Black Reef	2110	2310	2510	—	Louw (1955).
Western Reefs	1690	2010	2390	—	Louw (1955).
Marievale	2220	2170	2100	—	Louw (1955).
Blijvoorvitzicht	2110	2080	2070	—	Louw (1955).
Babrasca	1910	2060	2250	—	Louw (1955).

alteration involving the differential loss of lead, uranium and thorium is not a normal continuous process throughout the life of a mineral. Even though a mineral specimen is structurally capable of differential loss of lead, uranium or thorium, it will not undergo alteration unless the proper external conditions are existent.

(2) The degree of discordance is essentially independent of the age of the mineral. The variation in the 207/206 ages from different pitchblende samples from the same deposit proves that the major alteration did not occur recently. Therefore this discordance can not be attributed to supergene effects. Where a sample is weathered as in the case of the Katanga curite analyzed by Nier (1941), the age pattern can be reversed. For this to occur the mineral usually exhibits secondary uranium minerals.

(3) The fact that the 207/206 ratios of the radiogenic component of the lead isotopes in galena and clausthalite associated with pitchblende are closely grouped suggests that lead loss occurred during certain discrete events or intervals (Eckelmann and Kulp, 1956) and was not a continuous process. Temperature changes have been suggested as the most likely cause (Eckelmann and Kulp, 1956) but certain chemical environments may be required.

(4) Uraninite shows the age pattern $Pb^{206}/U^{238} < Pb^{207}/U^{235} < Pb^{207}$

$/Pb^{206}$. It also shows the apparent age relation of $Pb^{208}/Th^{232} < Pb^{206}/U^{238}$. Even if the uranium lead ages are concordant within the experimental errors, as is the case with the Viking Lake and the two Black Hills specimens, the Pb^{208}/Th^{232} ages show evidence of lead loss. Therefore the Pb^{208} is in a different structural environment than the Pb^{206} and Pb^{207}. The Wilberforce samples show a discordance slightly outside the experimental error but the age pattern is consistent with other uraninites. The ages for the one Wilberforce sample analyzed by Nier (1941) which show $Pb^{206}/U^{238} > Pb^{207}/Pb^{206}$ are actually within the experimental errors and the particular pattern is possibly the result of a slight error in the lead analysis. If the lowest lead analysis reported for this sample is used the Pb^{208}/Th^{232} age is lowered by about 40 m.y. The Wilberforce uraninite age pattern does not preclude the alteration having been fairly recent but more data may alter this conclusion. If the 207/206 ages of 1085 m.y. and 1012 m.y. are outside of the experimental error, this is evidence for lead loss in the past.

(5) The 208/232 age is lower than the 207/206 age in proportion as the 206/238 age is lower than the 207/206 age. This is shown best by the Huron Claim and Viking Lake samples. The Nicoll's Nob, Romteland and several Wilberforce samples are essentially concordant.

(6) Monazite shows two major types of discordance, i.e., $206/238 > 207/235 > 207/206 > 208/232$ and $207/206 > 207/235 > 206/238 > 208/232$. The particular conditions under which one or the other of these effects may be produced are not yet defined, but the alluvial monazite from Ene, India shows the greatest discordance suggesting that the Pb^{208} and uranium loss required for this discordance may be supergene, whereas the other pattern may develop under conditions of elevated temperature. It is clear from the monazite data on localities dated by other methods that the Pb^{208} is easily mobilized and that the uranium and its associated lead isotopes are removed in different relative amounts depending on the conditions. In most cases it would appear that the 207/206 age is closest to the true age. If the 207/206 and 208/232 ages agree this should be good evidence of the true age. In the case of the Goodhouse monazite, which yields concordant ages, acid leaching experiments by Tilton (1956) removed ratios of the uranium, thorium, and lead similar to those existing in the bulk mineral. Furthermore the sample was very homogeneous upon microscopic examination in contrast to the Quartz Creek monazite, which showed extensive orange-brown fillings in fractures.

Rubidium-strontium ages on the Southern Rhodesia localities reported by Aldrich, Wetherill, et al. (1956) and Huron Claim samples at Lamont show that in these cases of considerable alteration the 207/206 age is correct within the experimental error. The Quartz Creek, Colorado locality, however, appears to have a true age of 1350 ± 100 million years (Aldrich, Davis, et al. 1956) so that the 207/206 age of 1170 ± 50 is somewhat low indicative of lead loss early in the history of the mineral.

(7) Zircon shows a similar age pattern to uraninite, i.e. $Pb^{208}/Th^{232} < Pb^{206}/U^{238} < Pb^{207}/U^{235} < Pb^{207}/Pb^{206}$ except that the Pb^{208}/Th^{232} ag is even more sensitive to alteration. In this regard it is noteworthy that Tilton (1956) found a Pb^{208}/Pb^{206} ratio ten times larger in this acid wash than in the bulk Tory Hill zircon. Concordant results are obtained in the case of the excellent, large Ceylon crystals. The size of the crystal appears important. Zircons present as fine accessory minerals in a rock are more subject to alteration than coarse crystals. All of these samples were fresh and showed no evidence of surface weathering. Moreover most of the Pb^{208} at Wilberforce must have been lost subsequent to 390 m.y. ago. There appears to be no clear relationship between the extent of discordance and age. It would be of interest to analyze zircon from Bikita, So. Rhodesia to check this point.

(8) Samarskite shows a similar pattern to zircon. It should be noted these these samples were clean and glassy without a trace of alteration. The true age of the Spruce Pine samples is probably close to 350 m.y.

(9) Euxenite has a characteristic age pattern showing the Pb^{206} and Pb^{207} to be much more sensitive to removal than the Pb^{208} so that, at least for mild conditions, Pb^{207}/Pb^{206} age $=$ Pb^{208}/Th^{232} age which are probably close to the correct age.

(10) Microlite shows the apparent age relationships $Pb^{206}/U^{238} < Pb^{207}/U^{235} < Pb^{207}/Pb^{206}$. If the Harding Mine microlite and Petaca samarskite samples are actually the same age the greater sensitivity of samarskite to lead loss is indicated.

(11) Thorite, sphene and thucolite show a zircon-like pattern.

(12) Columbite-tantalite and xenotime show $Pb^{206}/U^{238} > Pb^{207}/U^{235} > Pb^{207}/Pb^{206}$ indicative of preferential uranium loss. The xenotime also shows evidence of Pb^{206} loss. Yttrotantalite is different from columbite in that the former shows $Pb^{206}/U^{238} < Pb^{207}/U^{235} < Pb^{207}/Pb^{206}$. It is different from the zircon and uraninite in that the uranium lead appears more readily leachable than the thorium lead.

Several localities for which more than one mineral has been analyzed are listed in Table 2. This compilation permits a comparison of the relative sensitivities to alteration under apparently identical conditions. The following conclusions appear warranted.

Under conditions of slight alteration e.g., Romteland, Norway, where the uraninite ages are essentially concordant, the uranium lead in euxenite is readily removed, but the thorium lead and lead ages are concurrent.

TABLE 2

Mineral	206/238	207/235	207/206	208/232	Reference
A. Romteland, Norway					
Uraninite	890±5	892±8	920±20	900±30	Lamont (unpublished).
Euxenite	485±5	560±7	910±20	920±35	Lamont (unpublished).
Thorite	740±6	760±8	830±25	495±30	Lamont (unpublished).
B. Huron Claim, Manitoba					
Uraninite	1564	1985	2475	1273	Nier (1941).
Uraninite	1860	2170	2505	1360	Lamont (unpublished).
Monazite	3217	2839	2590	1827	Nier (1941).
C. Quartz Creek, Colo.					
Monazite	1590	1420	1170	995	Tilton (1956).
Zircon	930	1130	1540	515	Carnegie Re. 1954–1955
Microlite	916	1055	1350	—	Tilton (1956).
Columbite-tantalite	1520	1470	1390	—	Tilton (1956).
D. Wilberforce Area					
Uraninite	1077	1050	1035	983	Nier (1939).
Uraninite	1015	1038	1060	—	Eckelmann & Kulp (1957).
Uraninite	1000	1015	1030	1010	Nier (1941).
Uraninite	1000	1020	1085	870	Wasserburg & Hayden (1955).
Uraninite	994	993	982	897	Wasserburg & Hayden (1955).
Zircon (1–2 mm.)	1030	1055	1090	390	Carnegie Re. 1954–1955.
Zircon (−200 mesh)	940	960	1015	—	Carnegie Re. 1954–1955.
Sphene	910	—	—	—	Carnegie Re. 1954–1955.
Sphene	—	—	1090	450	Tilton (1956).

This may be the explanation for the low chemical ages on euxenite in the Grenville Province reported by earlier workers. Thorite readily loses Pb^{208}. It is noteworthy that thorite is generally found outside of radioactive equilibrium (F. Senftle, private communication). The low Pb^{207}/Pb^{206} age for the Romteland thorite strongly suggests that the uranium lead removal occurred during a condition which did not affect the uraninite. This event or events could not have been recent but must have occurred in the geologic past.

The same mineral type in the same pegmatite may show quite different degrees of alteration, i.e. Huron Claim and Black Hills uraninites. Where uraninite is strongly discordant, monazite is also (Huron Claim). The Huron Claim data suggest a probable age for the deposit of at least 2600 m.y. The Pb^{207}/Pb^{206} ages from the uraninite reflect lead loss in the past. If uranium loss occurred in the monazite in the past, the 207/206 age would be too low.

Where other minerals such as uraninite (Huron Claim) and zircon (Quartz Creek) are strongly altered, monazite loses Pb^{208} as well as uranium.

Microlite has a stability similar to zircon under the same conditions.

The stability of zircon to alteration is similar to the stability of uraninite except that zircon can lose Pb^{208} more readily.

It is becoming clear that there are many factors which play a role in producing discordant uranium ages. Some of the effects can be predicted, measured and corrected, whereas others cannot be inferred quantitatively as yet. It appears that the Pb^{207}/Pb^{206} age is the best first approximation of the true age for all of these minerals and will almost always be minimal. The degree of uncertainty is related to the number of samples analyzed. If several samples of two or three mineral types can be analyzed from a given locality, it is possible to assign an age within fairly narrow limits. Thus despite discordance, the following ages are very likely: Romteland, Norway 920 ± 20 m.y.; Huron Claim, Manitoba 2600 ± 100 m.y.; Black Hills, South Dakota 1620 ± 20 m.y. and Wilberforce, Ontario, 1060 ± 20 m.y. Other age assignments can be made with a slightly larger error.

It remains to investigate the particular mechanism of removal in nature and to relate this quantitatively to the mineral structure.

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STUDIES OF THE SUBSTITUTION OF OH^- BY F^- IN VARIOUS HYDROXYLIC MINERALS*

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Abstract

The extent of replacement of the hydroxyl ions by fluorine in the type clay minerals and alumina hydrates has been studied by four separate methods: back-titration of developed alkalinity, wet analysis for fluorine, quantitative infra-red absorption spectroscopy of the OH band, and powder *x*-ray diffraction techniques. It has been found that relatively large amounts of fluorine (up to 50% of the total hydroxyl ions) are taken up by these minerals, the amount increasing with temperature. The magnitude of the exchange is similar in the type clay minerals, but in minerals such as diaspore, hydrogen bonding appears to strongly inhibit exchange. The question as to whether the fluorine replaces the hydroxyl in the lattice or decomposes the clay cannot be unequivocally answered. Positive evidence is found for the latter in the presence of cryolite in the highly fluorinated products, but in general, stoichiometric exchange may be the predominant reaction.

Introduction

Fluorine is the twelfth most abundant element in igneous rocks and what is perhaps more significant is that it ranks third among the most abundant anions (after O^{2-} and OH^-). Considerable experimental work has been done to determine the distribution of the most abundant cations among various crystalline phases as a function of composition, temperature and pressure with oxygen as the common anion. Recently such work has been extended to include hydroxyl as a component anion in the crystalline phases which were being studied. In contrast with this, very little experimental work is at hand which concerns the relationships among these phases in the presence of fluorine. Fluorine is a good example of a dispersed element occurring in a variety of the most common minerals (Barth, 1947) and forming only one fairly common "ore"—fluorite, CaF_2. In its dispersion it substitutes for $(OH)^-$ and only rarely for O^{2-} with corresponding loss of cation valence. Thus, one might expect that fluorine should be considerably more abundant in sedimentary rocks than in igneous or metamorphic rocks. This however, does not appear to be the case from the scanty data which are available. Rankama and Sahama (1950) give 140 gm. of CaF_2 per ton as the content in soils, although some bentonites have been reported with as much as 7,400 gm. F per ton.

In the clay minerals themselves which permit such a wide variety of cation substitution, one would expect that the chances for anion replacement of $(OH)^-$ by F^- would be particularly favorable. The experimental

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work to date on anion replacement is limited. Dickman and Bray (1941) in an earlier study demonstrated that large amounts of OH are released into solution when kaolinite is equilibrated with NH_4F solutions even at room temperature. Romo (1954) confirmed this finding by the use of infra-red spectra, and attributed this OH release to exchange of lattice hydroxyl by F^-. After this study had been initiated, Samson (1952) reported similar results but attributed his "adsorption" of fluorine to initial bonding to the aluminum of the lattice followed by breakup of the lattice by splitting off of $(AlF_6)^{-3}$ groups. No attempt was made to explain the nature of the fluorinated clay phase nor was mention made of the disposition of the $(AlF_6)^{-3}$ radicals. There were two quite different (though not mutually exclusive) explanations of the "adsorption" of F and the release of OH from clays. The first is the simpler one: stoichiometric anion exchange of fluorine for hydroxyl. In the second, solutions of neutral fluorides are presumed to react with and "decompose" the clay minerals with a resultant formation of various solid complex fluoride phases and the release of OH ions into the solution. In support of the former view, it should be mentioned that fluorine and hydroxyl appear to be in the proper relationship to each other as far as ionic size, charge and polarizability are concerned to make for efficient exchange. Moreover, in micas and amphiboles this substitution is well-known. In fact the more recent analyses show that fluorine is perhaps more abundant in these hydroxylated phases than the earlier analyses had suspected. However, this exchange may not take place to any great extent at low temperatures. Evidence for the second alternative of "decomposition" would be found in the formation of new phases or the presence of the clay cations in solution. Samson (1952) showed that small amounts of Al^{3+} were detectable in solution showing that this decomposition had taken place to some extent. In the present study a variety of analytical methods was employed in an attempt to arrive at more definite and quantitative data describing the exchange or decomposition of hydroxyl clays in neutral fluoride solutions. The effect on the fluorine absorption of the structure of the clay phase of its cation content and of the nature of the contained hydroxyl was also examined.

EXPERIMENTAL

1. *Materials Used*

Specimens of kaolinite, chrysotile, muscovite, boehmite, and diaspore were selected from well-established sources and their purity was checked by examination under the petrographic microscope and by *x*-ray diffraction. Each sample was fractionated by sedimentation to give $<1\mu$ *e.s.d.* particles. As supplementary information, it was also established by means of infra-red spectroscopy that each one of them gave an easily distinguishable $(OH)^-$ band. In selecting these minerals, representatives of several different major structural groups were thereby investigated: two- and three-layer silicates, dioctahedral and trioctahedral minerals, minerals with and without hydrogen bonding. The samples used were as follows: kaolinite, API No. 4 from Macon, Georgia; muscovite from Spruce Pine, North Carolina (well-formed single crystals); chrysotile from Thetford, Quebec; boehmite—synthetic (prepared hydrothermally at 250° C. and 10,000 psi pressure), and diaspore from Mexico, Missouri.

2. *Methods of Investigation*

In order to be able to arrive at some conclusions not only about the extent of exchange but also about the nature of the exchange process, the following different methods were used to follow the reaction:

A. Titration of Excess Alkalinity

In previous work on this problem by Dickman and Bray (1941) and by Romo (1954), it was established that if hydroxyl ions are replaced by fluoride ions when a neutral fluoride salt is added in solution to a hydroxylic silicate, an excess alkalinity is developed which can be titrated with standard acid. Following their procedure, one gm. samples of $<1\mu$ kaolinite, chrysotile, muscovite, boehmite, and diaspore were saturated with 0.4 N NaF and were washed with alcohol three times to eliminate the excess of salt. The pH of all the suspensions were 7.0 ± 0.2. These samples were then transferred to 400 ml. Erlenmeyer flasks to which there were added 50 ml. of standard solutions of NaF of varying molar strength. Then 10 drops of bromothymol blue indicator were added to each flask. The color indicated that the suspensions were at neutrality. It was noticed, however, that as time went on, the suspensions became alkaline as indicated by the appearance of a dark blue color. The excess alkalinity was titrated back to pH 7 with standardized 0.10 N HCl. From time to time small amounts of fluoride solution were added to each flask with the purpose of keeping the concentration of fluoride in the suspension constant. Three series of experiments were carried out:* (1) at room temperature, (2) at 60° C., and (3) by bringing the contents of flasks to boiling before each titration was performed. The titration data are presented in Figs. 1, 2, and 3 where m. eq. of $(OH)^-$ released per 1.00 gm. of solid phase are plotted as a function of time.

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* In addition several different types of blanks were run to check the effect of the beaker material, the effect of the NaCl formed on titration with HCl, et cetera. No significant alkalinity was found to be due to any of these causes considered.

In Fig. 1 the effect of concentration of F^- in the solution on fluorine absorption by kaolinite at one temperature (25° C.) is shown graphically, and in Fig. 2 the exchange in boehmite, kaolinite, and muscovite is compared in runs at 60° C. The titrations were carried out for a period of nearly three months at the end of which the reactions were proceeding very slowly. The marked influence on fluorine absorption of concentration of F^- in the solution and of the increase of temperature (i.e., kaolinite in 0.5 N solution) is noteworthy. The increase of OH release with concentration would appear to be against the "purely-exchange" phenomenon hypothesis since in that case at equilibrium, in the presence of an *excess* of fluoride ions the same final product should be attained at any one temperature. It may, of course, be contended that three months is not sufficient for the attainment of equilibrium and that in infinite time the curves would all meet.

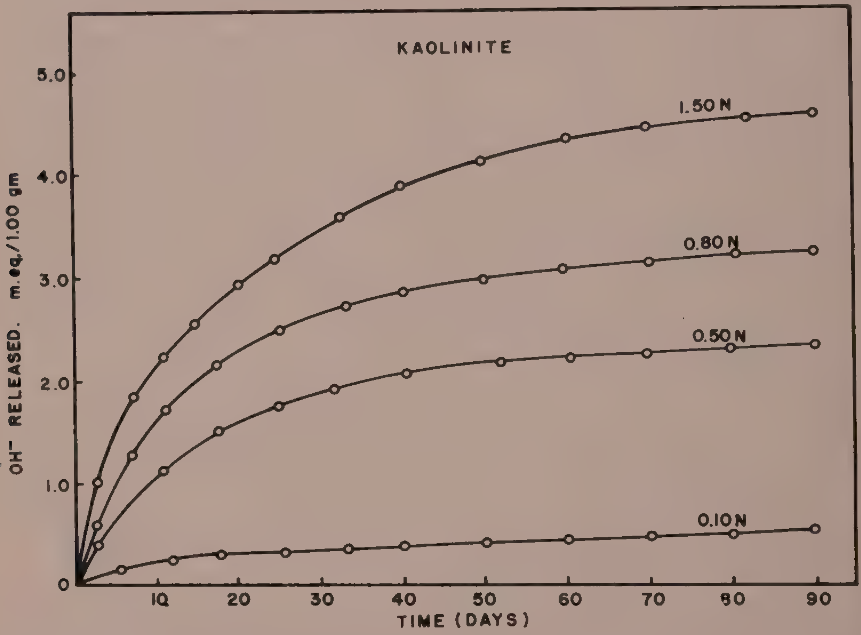

FIG. 1. Cumulative amount of $(OH)^-$ (in milliequivalents/gms. of clay determined by direct titration) released into solution by reaction between kaolinite and dilute NaF solutions of varying concentration. This series was run at room temperature.

In considering these titration data due regard must be had for the possible buffering action of the phases involved. However Romo (1952) has shown that the buffering capacity of the chief clay minerals at neutrality is only of the order 0.01 pH units and may therefore be neglected. The formation of complex ions and other side reactions producing $(OH)^-$ ions may also influence these data and these are discussed in a later section.

B. Analysis for Fluorine

The second method chosen for a study of the extent of reaction was direct analysis for F in the final product. After the reaction rates had decreased considerably (usually after about three months) the solid phase was separated from the fluoride solution by centrifuging. To achieve a complete removal of the fluorine the suspensions were centrifuged twice with distilled water and three times with 95 per cent ethyl alcohol. The fact that all the free fluorine has been removed was established on blanks as follows: Samples of 0.5 gm. of each of kaolinite and chrysotile were shaken with 50 ml. of 1 N NaF for ten minutes, then they were left standing for one hour. After this the solid phase was separated by centrifuging several times with water and 95 per cent ethyl alcohol. The analysis for F^- in the solid phase indicated that five wash-

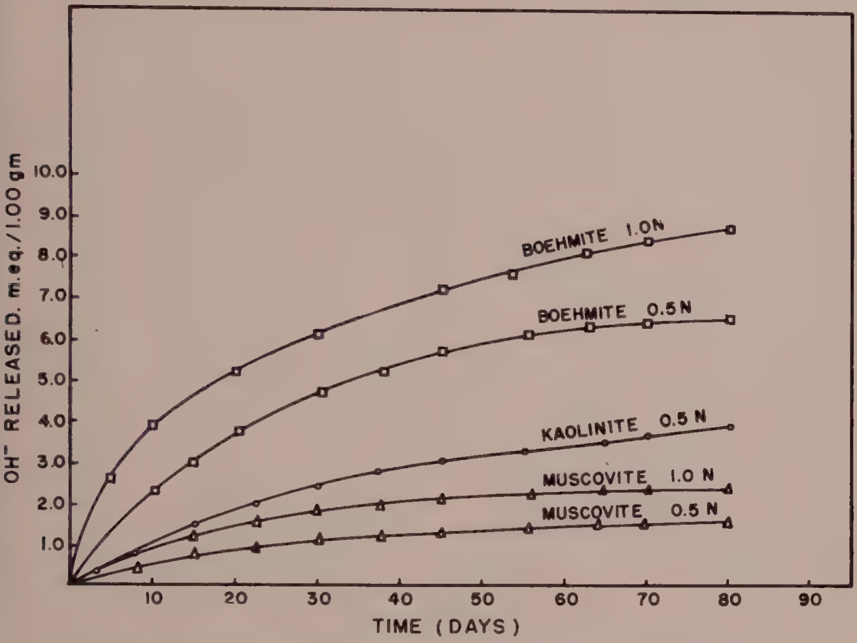

FIG. 2. Comparison of amounts of $(OH)^-$ released by different minerals in contact with NaF solutions of indicated concentration. This series was run at 60° C.

ings as given above were enough to remove completely all the free fluorine.

In the analytical determination of fluorine use was made of Willard's reaction (1933) as modified by Armstrong (1933). The distillation of fluorine from a water-$HClO_4$ system in silicates was found to give unsatisfactory results. Invariably it was found that the recovery is incomplete. Therefore a series of extraction tests with $HClO_4$-H_2SO_4 mixtures were made. It was found that use of 20 ml. of acid (2V) H_2SO_4-(8V) $HClO_4$ per 50 ml. of water gave the best results. The final procedure evolved is as follows:

Reagents:

Thorium nitrate: Dissolve 7.000 gm. of $Th(NO_3)_4 \cdot 4H_2O$ in one liter of water.

Indicator: Dissolve 0.100 gm. of sodium alizarin sulfonate in 100 ml. of water.

Buffer: Dissolve 10.00 gm. of CH_2Cl-$COOH$ and 2.20 gm. of NaOH in 100 ml. of water. The pH of this buffer should be adjusted to 3.80, adding either acid or base as required.

Standard NaF solution: Dissolve enough oven-dried salt (c.p. grade) to give 1 mg. F/ml.

Acid mixture: Mix H_2SO_4 and $HClO_4$ in the proportions of 2:8 by volume.

Procedure:

Fuse sample of fluorine-containing silicate (0.10 to 0.20 gm.) with 0.5 to 1.0 gm. of Na_2CO_3. Extract by heating the crucible in water at 80° C. until the alkaline cake is dissolved. Transfer the solution to a distilling flask (total volume 500 ml.) provided with a dropping funnel containing water and a thermometer and distill at a temperature of $145° \pm 3°$ C. As the distillation proceeds at the rate of 3 ml./min., water is added drop-wise to maintain the composition constant. A volume of 100 to 200 ml. is distilled depending on the concentration of F in the sample. The distillates in every case are made up to volume and aliquots withdrawn for analysis.

To aliquot in 50 ml. volumetric flasks, add 10 drops of indicator and NaOH drop-wise until a pink color appears. Such color should turn yellow upon the addition of one or two drops of 0.1 N H_2SO_4 (pH 3.6). Then add three ml. of buffer and make up to volume with water. Transfer the contents to a 250 ml. beaker and titrate with standard $Th(NO_3)_4$ solution until the pink color just appears. A blank is carried for any correction if needed. A standard curve was plotted by distilling the fluorine from fused kaolinate which contained known amounts of fluorine. An overall estimation of errors indicates that the accuracy of determinations is within $\pm 2.0\%$ in the range of 0.1 mg. F to 5 mg. F.

The comparison of analytical results shown in Table 1 indicates that there is reasonable agreement between m. eq. of $(OH)^-$ released and m.

TABLE 1. RELATION OF M.E. OH^- EXCHANGED BY F^- IN VARIOUS MINERALS

Mineral	Treatment	m.e. OH/gr.	m.e. F/gr.	Presence of Other Phase
Kaolinite	0.10 N (RT)	0.48	0.54	
	0.50 (RT)	2.20	2.36	x
	0.80 (RT)	3.22	3.27	x
	1.50 (RT)	4.50	4.67	xx
	0.50 N 60° C.	3.90	4.06	x
	1.50 N 60° C.	7.50	7.67	xx
	1.0 N Boiled	2.65	2.77	
Muscovite	0.10 N (RT)	0.11	0.13	
	0.50 N (RT)	0.70	0.76	
	0.50 N 60° C.	1.50	1.58	
	1.00 N 60° C.	2.30	2.23	x
	1.00 N Boiled	3.10	2.88	x
Chrysotile	0.10 N (RT)	0.42	0.53	
	0.50 N (RT)	1.72	1.90	
	1.00 N Boiled	3.42	3.55	
Boehmite	0.10 N (RT)	0.12	0.16	
	0.50 N (RT)	0.31	0.50	
	0.50 N 60° C.	6.50	6.84	x
	1.00 N 60° C.	8.60	9.26	xx
Diaspore	0.10 N (RT)	negligible traces		
	0.50 N (RT)	0.75	0.84	xxx

eq. of F^- found in the solid phases which may suggest that the substitution of $(OH)^-$ by F^- is stoichiometric.

C. Infra-red Spectroscopy

The use of infra-red spectroscopy in elucidating the molecular structure of organic compounds has proved to be very useful, especially in cases where the detection of functional groups becomes essential. In studies of anion exchange, such as that of the substitution of $(OH)^-$ by F^- in layer silicate structures, infra-red spectroscopy provides a possible means of actually detecting changes in $(OH)^-$ concentration. Romo (1954) used this method to show that fluorine replaces lattice hydroxyls in kaolinite, and it was used here as one of the means of studying the variations of $(OH)^-$ content of the solid phase as a result of replacement by F^- in various minerals. For quantitative work with powders the KBr pressed disc technique is satisfactory and this was used throughout. The I.R. absorption spectra were recorded with a double-beam Perkin Elmer model 21 spectrometer using a slit opening of 8.40μ and slow scanning.

The variations in hydroxyl content were determined by the method of integration of areas. However some of the absorption bands recorded contained actually a band corresponding to hydroxyls ($\lambda = 2.75\mu$) and an overlapping weaker band at $\lambda = 2.95$, which is often attributed to "free water." Thus, prior to integrating the areas, the contribution of the overlapped free water band has to be eliminated. This was done in an approximate but simple manner by symmetrical extrapolation of the band at $\lambda = 2.75\mu$. An error limit of ±3% was found between the duplicate runs of the same sample which is not high if one considers the number of factors which can contribute to this error.

TABLE 2. COMPARISON OF ANALYTICAL RESULTS OF PERCENTAGES OF EXCHANGE OF $(OH)^-$ BY F^- IN VARIOUS MINERALS

Mineral	Treatment	Titration	F^- Kaolinite	I.R. Analysis
Kaolinite	0.1 N (RT)	3.27	3.68	4.0
	0.5 N (RT)	15.00	16.20	17.0
	0.5 N 60° C.	22.00	23.20	26.0
	1.5 N 60° C.	48.70	49.20	53.0
Muscovite	0.1 N (RT)	2.32	2.75	3.0
	1.0 N 60° C.	48.30	46.80	42.0
	1.0 N Boiled	64.50	61.00	59.0
Boehmite	0.5 N 60° C.	38.80	41.00	25.0*
	1.0 N 60° C.	51.50	61.00	34.0*

* The anomalous values here must be due in part to the fact that the OH absorption in boehmite is spread out over several bands.

The results converted to percentages are shown in Table 2 and are also compared with the data obtained from the $(OH)^-$ titration and fluorine analysis in Fig. 3 and Table 2. The agreement among the three methods is good, showing that amounts of F^- detected are equivalent to the amounts of $(OH)^-$ released and also correspond to the amount of $(OH)^-$ lost by the solid phase.

D. *X*-ray Diffraction

One of the limitations of each of the preceding three methods is that although each provides a measure of either the loss of $(OH)^-$ or the presence of F^- in the "total solids" there is no prima facie evidence that the fluorine is actually being exchanged for $(OH)^-$ in the lattice concerned. However the agreement among the data (see Fig. 3) is such that the exchange concept would appear reasonable. *X*-ray diffraction methods might provide such first-hand evidence by establishing both the absence or presence of extraneous phases and by showing the gradual and continuous shift of spacings characteristic of solid solutions. In this, of course, the close similarity in ionic radii of F^- and $(OH)^-$ renders the method insensitive at best.

Powder *x*-ray diffraction patterns were therefore used to check the phase content of the product after exchange, every sample being so examined. A high angle Norelco or G.E. diffractometer with filtered CuK radiation was used for this purpose, with hollow aluminum slides, which were packed to avoid excessive orientation and eliminate errors of eccentricity. With respect to the determination of the presence of new phases in the solids left after saturation for three months, it was found that in most cases in which more than two m. eq. of $(OH)^-$ had been exchanged per gram of sample it was possible actually to detect the powder pattern lines of a new phase, cryolite. This same phase was found in all the samples which contained an extraneous phase. The minerals themselves showed no evidence of decomposition, even in those cases where half the hydroxyls had been replaced. This, of course, is a qualitative measure, but no evidence was found for the diminution or change of intensities nor for the formation of any other layer silicates. The quantitative estimation of the Na_3AlF_6 formed presents a very difficult problem which cannot be solved directly except in a rough manner and under the limitations of several unverifiable assumptions.

The evaluation of the amounts of Na_3AlF_6 formed was obtained by running a set of standard mixtures of kaolinite with varying concentrations of Na_3AlF_6. The variation in intensity of the peak at 2.76 Å was found to be related to concentration linearly. Thus the concentration of Na_3AlF_6 in the various samples was estimated by measuring the intensities of this peak and referring that to the working curve. In this way it was found that the concentrations of Na_3AlF_6 varies from traces up to 10 per cent. This estimate can only err on the low side. Some (if not much) of the Na_3AlF_6 may be of too fine a size to contribute to the Bragg diffraction. The fine particle size of the cryolite which formed is not the same as that used in the standardizing runs, and this may also vitiate the results.

The second aspect of the *x*-ray data with which we were concerned was the possibility that the cell dimensions, and hence spacings in the pattern, would show a regular shift as a function of the F^- content. Since precise data could most easily be obtained for the basal spacings, these were measured carefully on the Norelco diffractometer at a scanning rate of 1/8° 2θ per minute giving reproducibilities to within .01°. No sufficiently significant shifts in spacing were found to enable any definite conclusions to be drawn. A very small increase in the d_{001} spacing of the most fluorinated muscovite was noticed amounting to 0.04 Å, but the change was so small as to make quantitative statements meaningless. The failure to obtain such quantitative cell dimension changes which could be correlated with the amount of fluorine exchanged eliminated one of the only methods capable of yielding unequivocal proof for the "exchange" hypothesis.

Discussion of Results

The most surprising feature of the results is the extent to which the reaction (either exchange or decomposition, or both) will proceed even at room temperature. The data obtained by titration of the excess alkalinity developed, which constitute a measure of the hydroxyl released, have been shown to be equivalent within reasonable experimental error

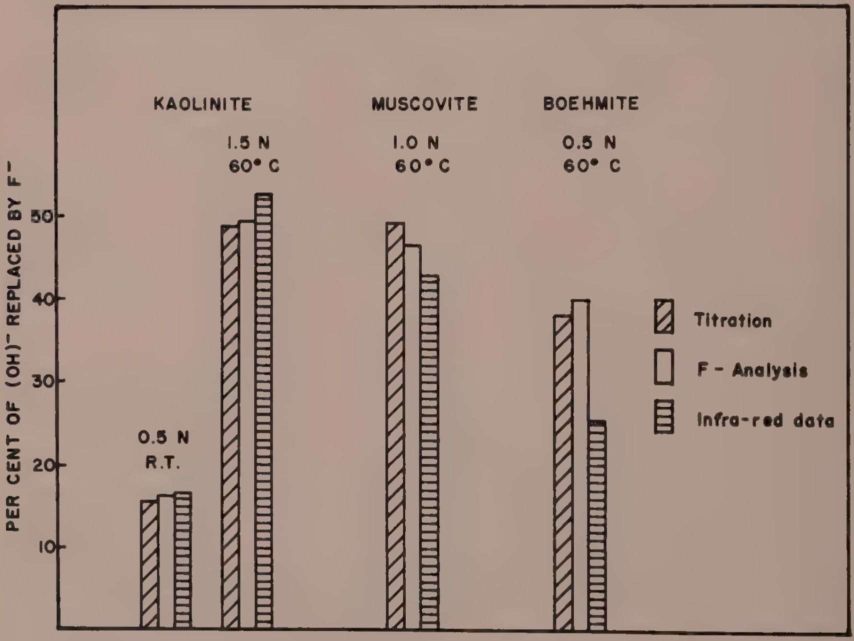

FIG. 3. Histogram comparing the extent of exchange as determined by the different methods used; the temperature and concentration of NaF is indicated for each of the cases selected.

to the amount of fluoride ion taken up in the total solid phase. Moreover, the infra-red spectra have established that the hydroxyl ions left in the mineral when estimated quantitatively account for the rest of the total hydroxyl content of the original mineral. The results of the three methods have been compared in a histogram in Fig. 3, and it is seen that the infra-red data tend to give a somewhat low value for the amount of "replacement," i.e., the amount of $(OH)^-$ found in the residue tends to be slightly high, which may be expected since strong adsorption at "fresh" surfaces formed during the reaction will give rise to errors in this direction. The general correlation is considered good.

From these data, however, one cannot decide unequivocally between the two possibilities which are available to explain the mechanism of the fluorine "take-up." The failure of the *x*-ray data to confirm the exchange hypothesis does not of itself speak for the decomposition, since it may be very reasonably argued that $(OH)^-$ and F^- are so similar in ionic properties that not much difference may be found in any case.* On the other hand if it were possible to rely on the estimates of the amout of Na_3AlF_6 formed, one would be led to conclude that the exchange reaction was the predominant one, since even in cases where half of the hydroxyls of the lattice have been released only about 5–10% of Na_3AlF_6 are estimated to have been formed. Further in these same samples where the fluorine take-up is considerable, one would expect a more definite effect on the absolute and relative intensities within the powder pattern for the clay mineral itself. Here a quantitative measure is impossible but no major changes were found in any case.

The two types of explanation can be expressed in greatly simplified form as follows:

Exchange: $Al_2Si_2O_5(OH)_4 + x\,NaF = Al_2Si_2O_5(OH)_{4-x}F_x + x\,NaOH.$

"Decomposition": $Al_2Si_2O_5(OH)_4 + 6NaF = Na_3AlF_6 + AlSi_2O_5(OH) + 3NaOH.$

The former equation is a reasonable view of what may actually take place while the latter is a highly idealized summary of the second alternative and of course does not really represent the actual process. It does indicate the direction of reaction and possible products. The elimination of aluminum and the increase in the Si/Al ratio in the clay phase will tend to develop 2:1 layer silicates from the 1:1 minerals, and from the former if the extent of fluoride take-up is large, zeolites or silica will have to be formed, since no layer minerals richer than the montmorillonites-micas are known. In the case above, it is seen that a coincidence leads to the formula of the residue being identical with that for pyrophyllite (as representative of the 2:1 montmorillonites and micas). Pyrophyllite would not, however, appear in the residue because the necessary activation energy is not available.

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* However, values published after completion of this study of 001 for F phlogopite and OH-phlogopite show a difference of the order of 0.17 Å.

Although the the actual process cannot be decided, some further information may be obtained from the time and temperature function of the extent of fluoride take-up. From the plots shown in Figs. 1, 2, and 3 it is possible to construct hypotheses regarding the possible rates of reaction. The titration curves presented therein show clearly that the release of $(OH)^-$ is dependent upon the concentration of NaF in solution which was kept constant in every case. From a cursory examination of the structure of these minerals, it is obvious that in most of them there are two types of hydroxyl groups: those which are on the outer edges of the "brucite" or "gibbsite" layers and are readily accessible, and those which are "inside" the lattice and are less accessible. Therefore, it is conceivable that two simultaneous processes may be taking place independently of each other—one involving direct exchange with the solution, and the other a diffusion process of fluorine ions into the lattice.

The nature of the reactions and specific rate constants can be evaluated by the usual treatment of these data. Such a treatment of the data has been performed for the kaolinite case. However the extent of subjectivism involved in fitting the curves does not justify the presentation of the numerical data. By such a procedure, one can arrive at fair agreement assuming two first-order reactions taking place simultaneously. The faster reaction rate constant would correspond phenomenologically to the exchange of the exposed surface hydroxyls. The slower one, possibly corresponding to the diffusion process of the fluorine into the inner layers, gave a rate constant approximately ten times as small.

The data also provide some indications of answers to our original questions. Thus the influence of the cation in the clay is seen to be minor since chrysotile and kaolinite give total reaction values in the same range. Morphology, particle size and surface area must also play only minor roles for these are quite different for chrysotile and kaolinite. Between the 1:1 (kaolinite family) and 2:1 (mica-montmorillonite groups) there is likewise no striking difference although the total exchange seems to be distinctly lower in the latter. This may be only a reflection of the lower total $(OH)^-$ content. Lastly with respect to the effect of hydrogen bonding in the hydroxyls, there does appear to be a definite difference between boehmite and diaspore. The diaspore samples showed the presence of large amounts of Na_3AlF_6 even at very low concentrations and at room temperature, and in the lowest concentrations of NaF they showed hardly any F^- take-up. On the other hand, boehmite shows an "exchange" of about the same magnitude as the layer silicates. This could be attributed to the marked hydrogen bonding in diaspore which, in effect, means that diaspore has no true hydroxyls that can be exchanged by fluorine.

In conclusion it may be stated therefore that there is extensive and fairly rapid transfer of F^- ions from solution to the solid phase when brought in contact with most layer silicates, and that this does constitute "fixation" of fluorine. However the mechanism of this fixation is left in doubt. No positive evidence for the replacement of the OH^- in the lattice by F^- was obtained. On the other hand, some evidence—which appeared quantitatively insufficient to account for all the F-fixation—was obtained for "decomposition" of the clay minerals and the formation of non-clay insoluble fluorides.

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BISMUTOTANTALITE FROM BRAZIL*

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ABSTRACT

Bismutotantalite from Acari, Brazil, has been found in light brown, rounded stream pebbles. Cleavage {101}, {010}. G=8.84 (meas.), 8.98 (cal.). Optically biaxial (+); $nX=2.388$, $nY=2.403$, $nZ=2.428$ for Li light. $2V=80^0$, $r<v$. $X=a$, $Y=b$. Analysis gives: Bi_2O_3 48.98, Sb_2O_3, 1.76, Ta_2O_5 46.45, Nb_2O_5 1.26, Fe_2O_3 0.94, SiO_2 0.16, ZnO 0.38, MnO 0.11, Ign. loss 0.62. Total 100.66. Formula: $4[(Bi,Sb)\ (Ta,Nb)O_4]$. The unit cell dimensions: $a_0=4.97$ Å, $b_0=11.80$, $c_0=5.66$; $a_0:b_0:c_0=0.4219:1:0.4801$. Space group: *Pcmn* or *Pcn.*

INTRODUCTION

Bismutotantalite, $Bi(Ta,Nb)O_4$, was described by Wayland and Spencer (1929) from Gamba Hill, southwest Uganda, Africa. Here it occurred in a pegmatite with black tourmaline and small amounts of cassiterite. To the present time this has remained its only locality.

In 1954 Mr. George W. Tower sent a mineral specimen to Harvard with a partial chemical analysis which identified it as bismutotantalite. The specimen was a rounded stream pebble two inches in diameter, a fragment from a single crystal. It is a light brown color, and except for several small veins of iron oxide through it, is extremely homogeneous. Several additional rounded pebbles have recently been received but most of the data reported here were obtained on the single original specimen. This material came from Acari in northeastern Brazil in the Campina Grande area. Here it occurs as a placer mineral over a rather wide area, for rounded pebbles of it have been found in the beds of several streams many kilometers apart. Prospecting failed to yield the mineral in commercial quantity, although at one place 50 kilograms were found. It is believed by Mr. Gert Schroeder, in charge of the prospecting, that the bismutotantalite ". . . was already a placer at the end of the first of the two erosion periods of the Brazilian shield as described by Johnson (1945). The second erosion destroyed this part of the old peneplane and dispersed the content to placers over a much larger area, where we find it to-day."†

PHYSICAL PROPERTIES

The Brazilian bismutotantalite bears little resemblance to the original material from Uganda, and familiarity with one would not aid greatly the determination by inspection of the other. A comparison of the physical properties of bismutotantalite from the two localities is given in Table 1.

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* Contribution No. 373, Department of Mineralogy and Petrography, Harvard University, Cambridge, Massachusetts.

† Private communication.

Bismutotantalite is orthorhombic. Wayland and Spencer (1929) described and figured large, well-formed crystals from Uganda having three directions of parting. No crystals of Brazilian bismutotantalite are available but the pebbles when broken show three well-developed cleavage directions. One perfect cleavage is at right angles to the other two. These lesser but distinct cleavages make an angle of 82°50′ with each other as measured on the reflecting goniometer. This compares favorably with the angle of 82°42′ between two "parting" directions as given by Wayland and Spencer. Orienting bismutotantalite to conform with Palache's (1940) orientation of stibiotantalite, this angle identifies the form as {101}. The perfect cleavage is, therefore, {010}.

Wayland and Spencer (1929) give three values for specific gravity of bismutotantalite as obtained on three separate specimens. Two of these on analyzed material are: 8.06 and 8.44. They state that the higher value was obtained on "somewhat fresher looking material." The third determination, yielding a value of 8.15, was made by Max H. Hey at the British Museum. During the present study, determination of the specific gravity of the Uganda material using the Berman balance gave a value of 8.38. Specific gravity determinations were made on three stream pebbles of bismutotantalite from Brazil, yielding the values—8.72, 8.84, and 8.89. The value on the analyzed specimen was 8.84.

Table 1. Physical Properties of Bismutotantalite

	Brazil	Uganda
Morphology	stream pebbles	large prismatic crystals
Color	light brown	black
Cleavage	{010}, {101}	parting
Specific gravity	8.84	8.38
Hardness	5	5
Streak	yellow-brown	black
Luster	adamantine	sub-metallic

The Uganda bismutotantalite is black and quite opaque in thin section. It is partially metamict. *X*-ray powder photographs, taken before and after heating to 800° C. in both air and in vacuum, show that heating produces a marked increase in crystallinity. Fragments heated in air turned a light yellow with a waxy luster and became translucent. When heated in vacuum the mineral remained black and opaque. The Uganda bismutotantalite is slightly radioactive and an analysis by the U. S. Geological Survey gives 0.061 per cent U_3O_8.* Although the amount is small, this uranium undoubtedly accounts for the metamict state. If the uranium is present as U^{+4}, it may also account for the opacity of the mineral since it is a powerful pigmenting agent. Moreover, the color change from black to yellow on heating is the type one would expect on a change from U^{+4} to U^{+6}.

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* Since the valence state was unknown, the uranium was reported by the analyst as 0.052 per cent U and here calculated as U_3O_8.

A differential thermal analysis of the Uganda bismutotantalite showed that a marked exothermic reaction takes place at 413° C. A similar run on the Brazilian material showed no thermal reaction. This apparently is the temperature at which recrystallization and possibly oxidation takes place. When heated at 350° C. for thirty minutes, there was no change in color nor in the *x*-ray diffraction pattern. However, when heated at 420° C. for thirty minutes, the mineral turned yellow and showed the same increase in crystallinity as when heated to 800°. Kerr and Holland (1951) point out that a differential thermal analysis of davidite gives an exothermic peak and indicate that this may be characteristic of metamict minerals.

Table 2. Optical Properties of Bismutotantalite

Brazil		Uganda	
	n_{Li}		n_{Li}
$X=a$	2.388	$X=a$	2.395
$Y=b$	2.403	$Y=b$	2.408
$Z=c$	2.428	$Z=c$	2.426
Opt.(+)	2V=80°	Opt.(+)	2V=85°
	$r<v$		$r<v$
	G=8.84		G=8.51

When heated to 800° C., the specific gravity of the Uganda bismutotantalite increases from 8.37 to 8.51. This increase in specific gravity on heating is characteristic of many metamict minerals as pointed out by Pabst (1952).

Penfield and Ford (1906) describe strong pyroelectric effects in stibiotantalite with [010] the polar axis in the orientation of Palache (1940). Because of the close relationship between this mineral and bismutotantalite, the same effects might well be expected in bismutotantalite. However, no pyroelectric or piezoelectric effects were observed.

The optical properties of bismutotantalite are summarized in Table 2. The measurements were made in sulfur-selenium melts. Those for the Uganda material are for the mineral after it was heated in air. It is opaque before heating.

CHEMICAL COMPOSITION

In Table 3 is given the chemical analysis of bismutotantalite from Brazil with the analysis from Wayland and Spencer (1929) of the "fresher looking material" from Uganda.

TABLE 3. CHEMICAL ANALYSES—BISMUTOTANTALITE

	Brazil		Uganda	
	1	1*a*	2	2*a*
Bi_2O_3	48.98	49.51	52.26	52.70
Sb_2O_3	1.76	1.78	0.04	.04
Ta_2O_5	46.45	46.95	40.12	40.46
Nb_2O_5	1.26	1.27	6.63	6.68
Fe_2O_3	0.94		0.11	
SiO_2	0.16			
ZnO	0.38	0.38		
MnO	0.11	0.11	0.12	0.12
Ig. loss	0.62		0.33	
Total	100.66	100.00	99.61	100.00

1. Analysis by J. Ito, 1955.
1*a*. Analysis #1 recalculated to 100 per cent.
2. Analysis by W. O. R. Wynn in Wayland and Spencer (1929).
2*a*. Analysis #2 recalculated to 100 per cent.

It will be noted from the chemical analyses that the Uganda bismutotantalite is lower in tantalum and higher in niobium than the Brazilian material. One would, therefore, expect it to have the lower density as is borne out in the specific gravity determination. However, the specific gravity of both minerals falls considerably below the calculated values. From Uganda: measured 8.51 (after heating), calculated 8.73; from Brazil: measured 8.84, calculated 8.98.

X-RAY STUDY

Rotation and Weissenberg photographs were taken of cleavage fragments of Brazilian bismutotantalite using copper radiation and nickel filter. Two orientations were used with the axes of rotation [010] and [100]. The dimensions of the unit cell determined from the Weissenberg photographs are given in Table 4. Inasmuch as bismutotantalite and stibiotantalite appear to be isostructural, the dimensions are given in the established orientation of stibiotantalite.

The unit cell dimensions of the Uganda bismutotantalite given in Table 4 were determined on the material before it was heated. After heating, the cell dimensions are the same as for the Brazilian bismutotantalite. The unit cell volumes are: before heating, 338.3 Å^3; after heating, 331.8. This is a decrease in cell volume of 2.1 per cent. The measured specific gravities show an increase (8.37–8.51) of 1.5 per cent.

TABLE 4. BISMUTOTANTALITE AND STIBIOTANTALITE UNIT CELL DIMENSIONS AND AXIAL RATIOS

	a_0	b_0	c_0	$a_0:b_0:c_0$
Bismutotantalite				
Brazil	4.97 Å	11.80	5.66	0.4219:1:0.4801
Uganda	5.00 Å	11.89	5.69	0.4205:1:0.4785
Stibiotantalite*				
Mesa Grande	4.92 Å	11.78	5.54	0.4173:1:0.4705

* Cell dimensions from Dihlström (1938).

From morphological crystal measurements Wayland and Spencer (1929) give the axial ratios of bismutotantalite from Uganda in the accepted orientation as: $a:b:c$—0.4266:1:0.4848.

Using the volume of the unit cell, V = 331.8 Å^3, and the measured specific gravity, 8.84, the molecular weight of the cell contents is calculated as M = 1795. There are thus four formula units per cell and the structural formula is: $4[(Bi,Sb)(Ta,Nb)O_4]$.

TABLE 5. *X*-RAY POWDER SPACING DATA AND WITH POSSIBLE INDICES FOR BISMUTOTANTALITE

Copper radiation, nickel filter, in Angstrom units

I	*d*(meas.)	*d*(*cal.*)	*hkl*	*I*	*d*(meas.)	*d*(*cal.*)	*hkl*
1	4.575	4.579	110	2	1.861	1.865	202
1	3.723	3.732	101	2	1.774	1.779	222
3	3.555	3.558	111	3	1.735	1.739	113
10	3.148	3.143	121	1	1.681	1.687	123
6	2.945	2.945	040	2	1.604	1.590	301
2	2.819	2.828	002	1	1.574	1.571	242
2	2.743	2.747	012	2	1.537	1.525	330
2	2.700	2.705	131	2	1.473	1.475	080
2	2.543	2.548	022	1	1.415	1.414	004
1	2.481	2.485	200	1	1.370	1.373	024
½	2.308	2.289	220	1	1.350	1.343	332
1	2.080	2.083	132	1	1.308	1.323	124
1	1.987	1.968	231	3	1.270	1.274	044
2	1.897	1.887	142	2	1.234	1.247	400

The space group extinctions from the Weissenberg photographs are the same as those given by Dihlström for stibiotantalite and lead to the space group *Pcmn*. This is on the assumption that the crystal class is rhombic dipyramidal as indicated by the absence of piezoelectricity. If, however, it is pyramidal, as its close similarity to stibiotantalite would indicate, the space group is *Pcn*.

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THE WURTZITE-GREENOCKITE SERIES*

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Abstract

Specimens from Tsumeb, Southwest Africa, are found to be intermediate members in the wurtzite-greenockite series. Green, brown and orange color varieties are described that have respectively Cd:Zn ratios: 41.5:58.4; 54.2:45.8; 57.6:42.4. A linear variation is shown from wurtzite to greenockite in specific gravity, refractive indices, and unit cell dimensions. All varieties fluoresce in the U.V. As in synthetic phosphors the peak of the luminescent band is displaced from blue toward red with increasing cadmium.

Introduction

The few available analyses of greenockite and wurtzite show for both minerals only slight variations from the theoretical compositions. Very little solid solution between the two minerals has been reported in spite of the fact that a complete series has been synthesized.

Through the kindness of Dr. G. Söhnge and Dr. B. H. Geier of the Tsumeb Corporation, several specimens from Tsumeb, Southwest Africa, containing minerals that carry appreciable amounts of both zinc and cadmium, were made available for study. These proved to be intermediate members in the wurtzite-greenockite series. On the basis of color the minerals can be separated into three distinct varieties: 1. orange, 2. brown, 3. green.

Occurrence†

The zinc-cadmium sulfides were found mainly in the 1940 and 1941 stopes near the west end of the steeply plunging pipe-like Tsumeb ore body between the 17 (1595 ft.) and 20 (1890 ft.) levels. The minerals showed up in noteworthy concentrations in the footwall portion of the main lens of high-grade ore that was about 30 feet wide. Assays from this particular zone averaged 13 per cent cadmium as compared with an average of 0.2 per cent in the mill heads of run-of-mine ore. The Zn-Cd sulfides were scattered through a lead-rich, zinc-deficient mineral assemblage containing moderate amounts of pyrite, tennantite, bornite, chalcocite and digenite. The orange variety showed a marked concentration in chert and shale, the brown variety mostly in pseudo-aplite, whereas no special preference was evident in the green variety. In order of abundance the brown sulfide predominated, the orange being subordinate, whereas the green variety occurred only sporadically; all three, however, were closely associated within the cadmium bearing zone which appeared to have escaped supergene effects.

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* Contribution No. 374 from the Department of Mineralogy and Petrography, Harvard University, Cambridge, Massachusetts.

† This statement of *occurrence* supplied by G. Söhnge.

CHEMISTRY

Although adequate amounts of the brown and green varieties were available, they both were so intimately mixed with other minerals, notably quartz, galena and pyrite, that it was impossible to separate a sample sufficient for chemical analysis that was free from impurities. Specimens containing these minerals were finely crushed and sizes minus 325–plus 400 mesh were separated. Initial separations were made using methylene iodide to remove fragments with specific gravity less than 3.30. The heavier portions were then separated with a Frantz *isodynamic separator.* Microscopic examination showed that, even with many passings through the separator, the majority of the grains had minute specks of impurities attached to them. Chemical analyses were made, therefore, on samples in which it was recognized that there were small amounts of galena, pyrite and quartz. Spectrographic analyses of a few milligrams of carefully hand-picked material free from visible impurities showed for all varieties the presence of copper and manganese

TABLE 1. CHEMICAL ANALYSES OF CD-ZN MINERALS, TSUMEB

	Green		Brown		Orange
	1	1*a*	2	2*a*	3
Cd	31.93	39.87	43.66	49.34	49.75
Zn	25.92	32.36	21.48	24.27	21.30
Ca	0.65	0.81	1.35	1.53	tr.
Mn	0.34	0.43	0.61	0.69	0.12
Pb	9.09		1.96		none
Fe	1.51		2.97		none
S	24.39	26.53	25.10	24.17	
Insol.	5.94		3.33		0.65
	99.77	100.00	100.46	100.00	
Atomic proportions					
Cd:Zn	41.5:58.4		54.2:45.8		57.6:42.4
Specific Gravity					
Meas.				4.50	4.53
Calc.		4.44		4.53	4.54

Chemical analyses by Jun Ito.

Analyses 1*a* and 2*a* recalculated to 100 per cent after removing Pb, Fe and sulfur for PbS and FeS_2.

but the absence of iron and lead. One seemed justified, therefore, in considering the iron and lead reported in the chemical analyses as due to the presence of pyrite and galena and that manganese and copper substitute for zinc or cadmium in the structure. The insoluble portion was considered to be quartz.

Although the orange variety was extremely limited, it was sufficiently coarse so that it was possible to hand pick 140 milligrams of the mineral free from impurities. On this small amount of material only the metallic elements could be determined.

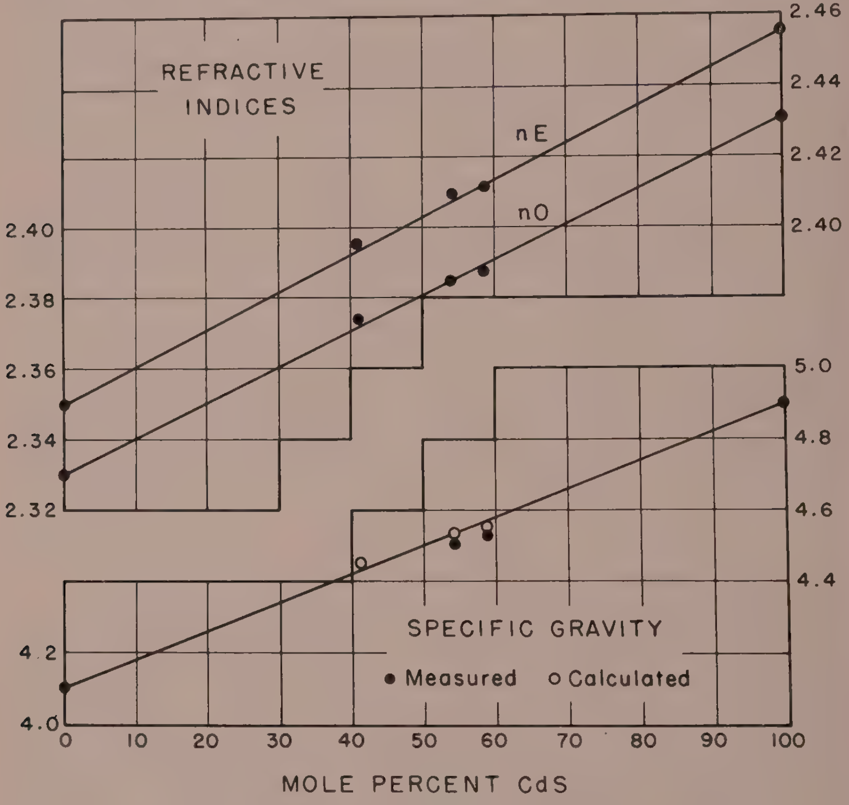

FIG. 1. Refractive indices and specific gravity, wurtzite-greenockite series.

PHYSICAL PROPERTIES

Both the orange and brown varieties show poor $\{11\bar{2}0\}$ and $\{0001\}$ cleavage, the same as reported for wurtzite. In addition, the orange variety also shows evidence of a poor $\{11\bar{2}2\}$ cleavage. No cleavage was observed on the green variety but because of the fine-grained nature of the material, this should not be considered as evidence of the lack of cleavage.

The specific gravities of the orange and brown varieties were determined on the Berman balance, using carefully hand-picked material. The specific gravities are: on 25 milligrams of the orange variety, 4.53; on 9 milligrams of the brown variety, 4.50. These values are plotted in Fig. 1 with the measured values of the specific gravity of wurtzite (4.1) and greenockite (4.9). Assuming that the change in specific gravity with composition is linear, the measured values given above should fall on the straight line. Both fall slightly below. The calculated values for the specific gravity are green variety, 4.44; brown variety, 4.53; orange variety, 4.54.

Optical Properties

Wurtzite, greenockite and the intermediate members in the series are all uniaxial positive. The refractive indices given in Table 2 vary with the composition as shown in Fig. 1. Refractive indices for wurtzite and greenockite are from Vol. 1, *System of Mineralogy* (1944); the others as reported are ±0.003.

TABLE 2. REFRACTIVE INDICES. WURTZITE-GREENOCKITE SERIES

	Wurtzite	41.5 CdS	54.2 CdS	57.6 CdS	Greenockite
nO_{Li}	2.330	2.374	2.382	2.388	2.431
nE_{Li}	2.350	2.395	2.405	2.409	2.456

Fluorescence

The literature on the fluorescence of the synthetic zinc-cadmium sulfide solid solution series is voluminous. Most of it is summarized in the books by Leverenz (1950) and Fonda and Seitz (1948). This solid solution series is of particular interest because of its use in the preparation of commercial phosphors. These are usually prepared, according to Kroger and Dikhoff (1950), by heating together pure ZnS and CdS with a small amount of an activator (Ag, Cu, Au, Mn) and a halide. The monovalent Ag^+, Cu^+, Au^+ substitute for the Zn^{++}. The halide serves a dual purpose. It acts as a flux and enters into the structure as anions Cl^-, Br^-, or I^- forming a coupled substitution. In this solid solution series the peak of the luminescent band is displaced from the blue toward the red end of the spectrum with increasing cadmium concentration.

In the minerals under consideration, the same phenomenon is observed as in the synthetic material. The fluorescent colors of the three members of the series are as follows:

Color of Mineral	Mole per cent CdS	Fluorescent Color
orange	57.6	orange-red
brown	54.2	yellow-orange
green	41.5	yellow

In an examination in ultra-violet light of 34 wurtzite and 42 greenockite specimens in the Harvard collection, no fluorescence was shown by any of them. This lack of fluorescence probably indicates, as do chemical analyses of greenockite and wurtzite, that there is normally little if any solid solution. Schroll (1953) in a study of the trace elements in wurtzite and sphalerite points out that the maximum amount of cadmium reported in wurtzite is three per cent and is normally less than one per cent.

UNIT CELL

X-ray powder photographs of the three varieties were indexed and from these the unit cell dimensions given below were calculated. Rotation and Weissenberg photographs were also taken of the brown variety, rotating the crystal about both the *c* and *a* axes. The 0-layer Weissenberg photograph taken about the *a* axis was carefully inspected for evidence of a multiple cell along *c* as described by Frondel and Palache (1950) for polymorphs of wurtzite. None was found and the structure is that of wurtzite 2H in the designation proposed by Ramsdell (1947) for silicon carbide.

The systematic extinctions shown on the single crystal photographs lead to the space groups $C6/mmc$ or $C6mc$. No crystal forms are present to aid in determining the symmetry but a strong piezoelectric response shows the space group to be $C6mc$, the same as in wurtzite and greenockite.

TABLE 3. UNIT CELL DIMENSIONS. WURTZITE-GREENOCKITE SERIES

	Wurtzite	Green var.	Brown var.	Orange var.	Greenockite
a_0	3.811 Å	3.958	3.995	4.006	4.142
c_0	6.234 Å	6.444	6.490	6.510	6.724

The unit cell dimensions of the series show a systematic change from wurtzite to greenockite, and, as in the other properties, vary almost linearly as shown in Fig. 2.

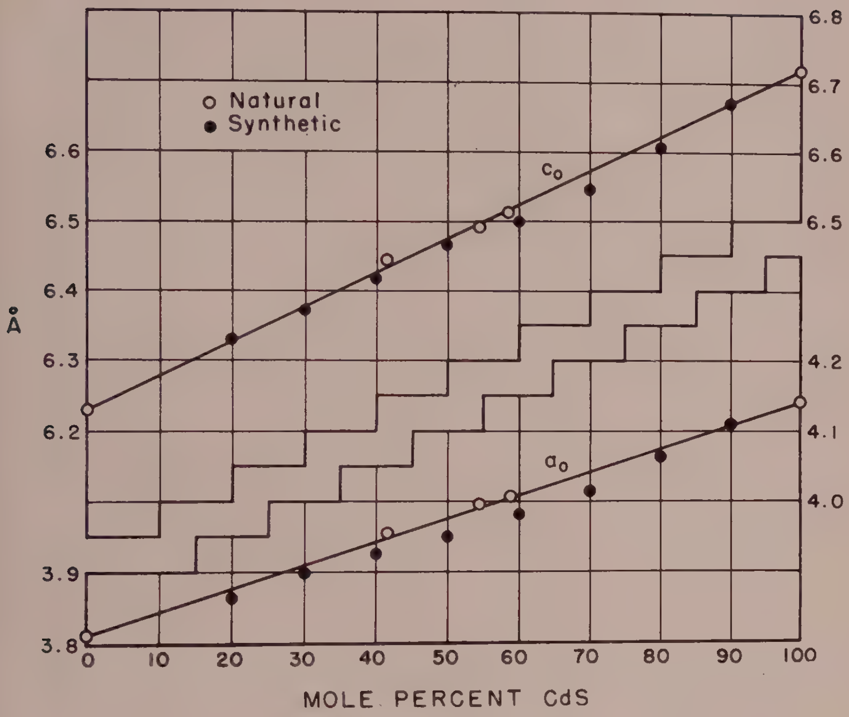

FIG. 2. Unit cell dimensions, wurtzite-greenockite series.

A series of zinc-cadmium phosphors synthesized by Dr. E. S. Rittner were available for study and comparison with the natural material. The dimensions of the unit cells of this series depart more from linearity than do those of the natural minerals as shown in Fig. 2.

TABLE 4. UNIT CELL DIMENSIONS. SYNTHESIZED ZINC-CADMIUM SULFIDES

Per cent CdS	20	30	40	50	60	70	80	90	100
a_0	3.863 Å	3.898	3.922	3.950	3.979	4.012	4.063	4.098	4.143
c_0	6.329 Å	6.373	6.418	6.464	6.498	6.545	6.604	6.677	6.729

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SOME PHYSICAL PROPERTIES OF NATURALLY IRRADIATED FLUORITE[1,2]

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Abstract

Five samples of purple fluorite found in association with radioactive materials, and a synthetic colorless control sample were studied and compared. Before and after heating, observations were made on specific gravity, index of refraction, unit-cell size, breadth of x-ray diffraction lines, and fluorescence. The purple samples became colorless on heating above 175° C. During the process, observations were made on color, thermoluminescence, and differential thermal analysis curves. There were strong correlations between the various physical properties, and it was found possible to arrange the samples in order of increasing difference in their physical properties from the control sample. This order apparently represents increasing structural damage by radiation; if so, it correlates with decreasing specific gravity, increasing index of refraction, broadening of x-ray lines, and increasingly strong exothermic reactions on annealing. The differences between the samples in index of refraction and x-ray pattern are largely eliminated on annealing. Annealing begins at 175° C.; thermoluminescence at lower temperatures is due to electrons escaping from the metastable potential traps, not the destruction of those traps which takes place on annealing.

Introduction

Purple fluorite is often found associated with deposits of radioactive material. Many workers have colored fluorite purple by exposing specimens to various sorts of ionizing radiation. It has also long been known that this purple color bleaches out on heating. The purple coloring has been ascribed to *F-centers*. These are regions of low potential energy in which electrons or ions are trapped in a metastable state, such that among the permitted increments of energy, there is a range corresponding to the absorption of visible light. Impurities may give rise to *F-centers* by providing permitted energy levels between those of the ordinary calcium fluoride structure, which normally has energy levels too far apart to permit electrons in the ordinarily filled orbitals to absorb visible light.

Omission of a fluoride ion would leave a gap surrounded tetrahedrally by positively charged calcium ions. Electrons may be trapped in the gap itself or in imperfections arising from the distortion caused by the gap. Or the gap may operate indirectly to trap electrons, as the various mechanisms that compensate for the charge of the missing ion—such as omission of cations or introduction of impurities of different charge—may themselves contribute to the formation of the "potential wells" in which electrons may be trapped.

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[1] Publication authorized by the Director, U. S. Geological Survey.

[2] Contribution No. 372, Department of Mineralogy and Petrology, Harvard University.

In short, any defects or imperfections in the structure that bring positive ions into a position such that electrons may be trapped between them may contribute to the purple coloring.

When irradiated fluorite is heated, the structure can readjust itself to the more stable state, eliminating defects, gaps, and areas of strain, and the coloration is destroyed.

Description of the Samples

Five specimens of fluorite collected from radioactive deposits were chosen from the Harvard collection. Their descriptions follow.

Sample F1 from Wölsendorf, Bavaria. The fluorite is dark purple-black in color, the purple tint being apparent only by direct comparison with the jet-black uraninite on the same specimen. It is so nearly opaque that its optical properties were very difficult to determine. It has some very poorly formed cleavages, consisting largely of concave areas of minute surfaces reflecting light in approximately the same position. The fluorite is riddled with minute cracks. The specimen also has some patches of reddish-brown feldspar and cavities and fractures filled with secondary uranium minerals. The sample of fluorite for study was taken from within 6 mm. of the edge of the uraninite. The fluorite is very brittle, shattering to a powder very quickly and easily during the grinding process. When ground or broken with a hammer, the fluorite gives out a very sharp odor ascribed by Hoffman (1937) to HF and ozone, the result of free fluorine liberated by radioactivity. The material has been given the name antozonite, after the supposed evanescent gas, antozone. Earlier names were Stinkstein and Stinkfluss (Hausmann, 1847).

Sample F2 from Wilberforce, Ontario. The fluorite consists of a rodlike mass about 3 mm. across, completely buried in a crystal of uraninite. The material is so dark that the contact between the fluorite and the uraninite could not be seen, although irregular cleavages did develop in the fluorite mass, marking out its approximate extent. The material is so nearly opaque that the index of refraction could not be obtained. Locally, there was a dull, red-brown powder in and on the fluorite. The entire sample was crushed and separated by sink-float methods.

Sample F3 from the Clark fluorspar mine, Cardiff Township, Ontario. The fluorite is dull, dark purple, brittle and minutely cracked. It occurs as inclusions in and interstitial to aggregates of uranoan thorite. Apatite and diopside are also present in the specimen. On being crushed, it gives off an odor similar to that of sample F1. Grains of microscopic size were translucent. The average distance of the particles of the sample from the thorite was about 5 mm.

Sample F4 from Nippissing Syndicate, Harcourt, Cardiff Township, Ontario. It consists of translucent fluorite, colored a relatively light purple red. Flat cleavage planes several millimeters wide appear on the surface of the specimen. The fluorite is associated with calcite, apatite, sphene, diopside, and widely scattered uranoan thorite. It is transparent under the microscope and gives off no noticeable odor when ground. The fluorite is several centimeters away from the nearest uranoan thorite crystal.

Sample F5 is colorless synthetic fluorite made by the Harshaw Chemical Company. It consists of fused reconstituted material from southern Illinois. Many of the physical properties of this material were measured with great precision by R. D. Allen (1950), who reported this as sample 38.

Sample F6 from Wilberforce, Ontario. It consists of reddish calcite with irregular microscopic patches of virtually opaque fluorite. The calcite is in contact with uraninite. Within

4 mm. of the uraninite, the calcite-fluorite mixture is blue rather than reddish. The calcite consists of alternate light and dark layers about 1 mm. wide, the dark layers containing more fluorite. The fluorite was recovered by treating the material with acid. The grains are very rough and irregular in shape and tend to form loose aggregates that make the powder very difficult to handle. The material selected for the sample was about 15 mm. from the nearest visible uraninite.

Many of the physical properties of the samples before heating show strong correlations between themselves. It is possible to arrange the samples in order of decreasing difference of their properties, in general, from those of the control sample. To illustrate these correlations, the data will be listed in this order. Starting with the one most different in its properties from the control sample, the samples are F2, F6, F1, F3, F4, and F5.

SPECIFIC GRAVITY

Specific gravity was measured by preparing a mixture of methylene iodide and acetone in which the material was just suspended. The density of the liquid was then obtained by weighing it in a tared 25-ml. volumetric flask.

The purple fluorite samples all had a specific gravity considerably less than the control sample. The range for a single sample was narrow, on the order of 0.007 or 0.008 gm./cm.^{3}. The values changed little with bleaching, indicating that the low specific gravity was due primarily to cracks rather than structural imperfections. According to Merwin (1911), the specific gravity of fluorite is 3.180±0.001.

TABLE 1. SPECIFIC GRAVITY OF FLUORITE SAMPLES

Sample No.	Before heating	After heating (1 hr, 600° C.)
F2	3.063±0.004	
F6	porous	
F1	3.093	3.088
F3	3.105	
F4	3.142	3.139
F5	3.180	

X-RAY DIFFRACTION

The samples were run at 0.25° per minute on an *x*-ray diffractometer, using nickel-filtered copper radiation. On the high-angle lines, a scale factor of 4, a multiplier of 1.0, and a time constant of 2 seconds were used. The samples were packed by hand into the aluminum holders against a glass slide taped to the front. No binder was used. The *x*-ray unit was run at 40 kv, 20 ma.

Three values were determined for each Kα_1 line: the Bragg angle (2θ) of the intersection of the axis of symmetry for the upper part of the peak with the background level; the height of the peak above background, in arbitrary chart units; and, as a measure of line broadening, the distance between the axis of symmetry and the pen trace on the low-angle side, at half the height of the peak. The low-angle side of the peak was used to avoid the interference of the Kα_2 peak.

TABLE 2. CELL CONSTANT OF FLUORITE SAMPLES, a_0 IN Å AT 25° C.
(CuKα_1=1.54050 Å)

Sample No.	Unheated	Heated (1 hr, 600° C.)
F2	lines too broad	
F6	5.4633	5.4636
F1	5.4631	5.4635
F3	5.4635	5.4633
F4	5.4634	5.4632
F5	5.4633	

The values for the cell constant calculated from each line were plotted against the Nelson-Riley function and extrapolated to $\theta=90°$ to give the final corrected a_0 value. The samples are virtually identical in cell size, and show no significant change with bleaching. The values in Table 2 can be summarized as $a_0=5.4633\pm0.0003$ Å at 25° C. Allen (1950) gives a value of 5.46295 ± 0.00010 Å at 20° C.

LINE BROADENING

The amount of structural imperfection is reflected in the width and height of the peaks. These values are also affected by the packing of the sample. Fortunately, the influence of the packing factor can be estimated.

TABLE 3. HEIGHTS OF PEAKS ABOVE BACKGROUND IN ARBITRARY CHART UNITS

Sample No.	(422) line		(531) line	
	Unheated	Heated (1 hr, 600° C.)	Unheated	Heated (1 hr, 600° C.)
F2	24	—	5	
F6	28	58	12	22
F1	29	46	11	15
F3	34	62	13	26
F4	51	58	19	30
F5	88		11	

If the differences are due entirely to the preparation of the sample, the width of the peak should vary as the height. If they vary inversely, as Tables 3 and 4 show, it can be assumed that the causes are of a structural nature. The (422) and (531) lines were selected for the tables because they are fairly intense high-angle lines. They represent spacings of 1.11 and 0.923 Å, respectively. For CuKα radiation, the values for 2θ are 87.3° and 113.0°.

TABLE 4. HALF WIDTH (LOW-ANGLE SIDE) AT HALF HEIGHT, IN HUNDREDTHS OF A DEGREE 2θ

Sample No.	(422) line		(531) line	
	Unheated	Heated (1 hr, 600° C.)	Unheated	Heated (1 hr, 600° C.)
F2	19		50	
F6	17	6	27	10
F1	15	5	24	7
F3	7	5	17	8
F4	6	6	7	6
F5	4		7	

The increase in line broadening (Table 4) in the unheated samples from F5 to F2 evidently has a structural basis and represents increasing strain and imperfection in the crystal structure.

Regardless of the starting point, the samples after heating give results similar to those of the least imperfect natural sample, F4, before heating.

INDEX OF REFRACTION

A double-variation apparatus such as described by Emmons (1928, 1929) was used to measure the index of refraction. All measurements were made with the monochromator set on the value for the sodium *D* line ($\lambda = 589$ mμ) as the temperature was varied from 25° to 40° C. Mixtures of amyl alcohol and mineral oil were used as the immersion media, the liquid being checked immediately in the Abbe refractometer that forms part of the equipment. Immersions of several dozen grains were prepared, and the stage was heated by circulating water until the immersion liquid reached and passed the range of index of refraction of the grains. The last indication of higher index and the first indication of lower index were noted; generally, the indices were about 0.0003 apart. Clearly, the sensitivity of the method is much greater than the accuracy, which is usually stated as ±0.001.

Allen's best values for the refractive index of fluorite (1950) were obtained on sample F5 by the minimum deviation method. They averaged 1.43385 for sodium light at 20° C. This value was used in checking the calibration of the Abbe refractometer.

Table 5. Indices of Refraction of Fluorite Samples
(λ=589 mμ.) Temperature=25° to 40° C.)

Sample No.	Before heating	After heating (1 hr, 600° C.)
F2	Opaque	1.4348
F6	1.4363	1.4325
F1	1.4389	1.4348
F3	1.4381	1.4349
F4	1.4357	1.4354
F5	1.4338	

Once again, the heated samples, with the exception of the anomalous F6, are very similar and show approximately the same value as the unheated F4. Among the unheated samples, except for F6, the index decreases along with structural damage, as shown by x-ray line broadening, in the series F2 through F5.

As the specific gravity decreases, the index of refraction increases. This is completely contrary to expectation; normally, as fewer ions are available to be polarized by the electromagnetic fields of the light waves, the index should decrease. A convenient empirical measure of the degree of interaction between the light waves and the light-induced dipoles of the material is provided by the *specific refractive energy* of Gladstone and Dale (1864). It is equal to $(n\text{-}1)/d$, where n is the mean index of refraction and d is the density. This function varies in a more or less straight line when substances are combined in different proportions.

The specific refractive energy decreases markedly down the series to F5, as Table 6 shows. The possibility that the change is due to trace elements was tested by calculating a theoretical value from the results of the spectrographic analysis (Table 7). The quantities present were assumed to be the upper limit of the bracket in which the elements were reported. The results of this calculation are listed in Table 6.

Table 6. Specific Refractive Energies of Four Fluorite Samples

Sample No.	Observed	Calculated
F1	0.1419	0.136 (15)
F3	0.1411	0.136 (16)
F4	0.1387	0.136 (35)
F5	0.1364	

The specific refractive energies for the trace-element fluorides were calculated from data on crystalline fluorides or silicofluorides.

Allen (1950), in his study of ordinary stable fluorite, reached the conclusion that trace elements were of only limited importance among the factors causing anomalous indices of refraction. This is even more certainly true of these irradiated samples, although trace elements may play a role in determining the susceptibility of the fluorite to structural damage.

The rise in index of refraction is apparently caused by the ions in metastable positions. They interact more strongly with the passing light waves than similar ions in stable positions, hemmed in by high potential barriers. When the fluorite is annealed, the specific refractive energy decreases toward that of the control sample.

Structural damage by radiation is usually associated with lower, rather than higher, indices of refraction. In most of the samples studied, however, the ions have been very much heavier than in fluorite. As in fluorite, there is a marked decrease in density, which results in a lower index, but counteracting effects would be very much more difficult to observe.

TRACE ELEMENTS

Spectrographic analyses were obtained on purified material in order to determine the role played by trace elements in the coloring or structural distortion of the fluorite. Adequate material could be obtained only from samples F1, F3, and F4. F1, the most strongly affected sample, is the purest CaF_2 of the three, and F4, the least affected, contains the largest amount of trace elements, on the order of five to ten times as much as F1.

Except for the absolute amounts, the lists of trace elements are very similar in the three samples, and are essentially those normally found in fluorites: Sr, Fe, Al, Mg, and rare earths. The Cr may have been introduced by instruments used in the grain picking.

TABLE 7. SPECTROGRAPHIC ANALYSIS OF THREE FLUORITE SAMPLES

Per cent	F1	F3	F4
Over 10	Ca	Ca	Ca
0.1–0.5	—	—	Al Si Sr
0.05–0.1	—	Sr Fe Y	Fe
0.01–0.05	Al Si Fe Sr	Si Al Mg	Y Mg
0.005–0.01	Y	—	—
0.001–0.005	Ba Cr	Cr Pb Yb	Cr
0.0005–0.001	Ti	Ba	Ba
0.0001–0.0005	Mg Yb	Ti	Ti Yb

Table 7 gives the spectrographic results as determined by K. E. Valentine of the U. S. Geological Survey. Fluorine was known to be present, and therefore was not determined. This determination requires a special process.

Behavior on Heating

When heated the samples pass through various shades of reddish purple and lavender until they become nearly colorless. By far the greater part of the bleaching, at temperatures over 300° C., is accomplished in the first few minutes. The rate of the process continuously decreases, and complete bleaching takes much longer. At 500°, the samples are completely bleached in an hour. At 470°, the samples are still light lavender at the end of 6 hours. Seventy hours is sufficient to bleach the samples completely at 400° C. but 18 hours at 370° was not. Sample F1 was completely bleached at 230° in 6 days. After 10 days at 185°, it became lighter in color and showed narrower *x*-ray lines. After the first few minutes the different samples being treated at the same temperature had virtually the same color, and thereafter they reacted the same way to further heating.

The increase in sharpness of *x*-ray line with progressive heating of sample F1 is shown in Table 8.

Table 8. Height and Breadth of (422) and (531) Lines at Different Stages of Bleaching of Sample F1

Time	Temp.° C.	Color	Breadth at ½ height		Height	
			(422)	(531)	(422)	(531)
Unheated		Purple-black	15	24	29	11
9 days	186	Purple	11	11	37	11
9 days plus 6 days	186 202	Light violet	9	14	39	14
6 days	230	Colorless	8	12	45	14
1 hr	600	Colorless	5	7	46	15

Differential Thermal Analysis

The samples were run on the differential thermal analyzer at Massachusetts Institute of Technology by Danforth Kelley. The equipment and methods have been described by Whitehead and Breger (1950). The samples were run in air, with the control sample, F5, in the other thermocouple well. Unfortunately some of the samples could not be purified completely before heating, and, when they were rendered colorless, patches of reddish material became visible in cracks and on the surface. This introduced an extraneous peak that interfered with the peak caused by the bleaching. Nevertheless, the two peaks could be separated graphically, if it is assumed that they are symmetrical.

All the patterns showed an exothermic peak at 360° C. when the temperature was increased at the rate of 20° per minute, and at 320° when the temperature rose 10° per minute. This peak plainly does not represent any critical point or stage in the reaction. The reaction rate increases as the temperature is raised and decreases as the reaction approaches completion. The peak represents the maximum rate. The pen trace begins to depart perceptibly from the center line at approximately 175° C. in all the runs. The height of the 360° peak in millimeters is given below, after graphical correction for the interfering peak in F3. Note that this is the same order as is shown by the tables of decreasing *x*-ray line broadening (Tables 3 and 4), and increasing index of refraction (Table 5).

TABLE 9. HEIGHT OF PEAKS AT 360° C. IN DIFFERENTIAL THERMAL ANALYSIS PATTERNS, RUN AT 20° PER MINUTE AGAINST SAMPLE F5

Sample No.	Height (in mm.)
F2	55
F6	16
F1	15
F3	12
F4	7

Under comparable conditions, the low-quartz high-quartz inversion gives a peak 46 mm. high at 573° C.

THERMOLUMINESCENCE

A borosilicate glass front for a muffle furnace was improvised from a beaker, so that the thermoluminescence of the fluorite samples could be observed in a darkened room. At 300° C., each individual grain flared up suddenly as it reached the threshold temperature for thermoluminescence. It would start glowing brightly, standing out clearly from the other grains already glowing. Within about 30 seconds, it would fade into the general glow which continued to dim as the material bleached. Raising the temperature would not revive the thermoluminescence to any great extent; in fact, it accelerated the decline.

The samples were observed from time to time by the usual room illumination. These subjective observations strongly suggest that the intensity of thermoluminescence is proportional to the rate of bleaching. This visible light represents a very small part of the energy released in going from the metastable purple state to the stable colorless state. It is probably caused by the fall-in of the entrapped electrons. By far the greater changes are associated with the destruction of the structural traps themselves.

The process is of course irreversible. No such effects are observed on heating already bleached fluorite.

The temperature at which thermoluminescence began could be determined fairly precisely. In the course of heating in a crucible on a hotplate, the entire sample was glowing 15 seconds after the first trace of thermoluminescence. The temperature was determined from a suspended mercury thermometer, the bulb of which was not in contact with the sides of the crucible.

As the temperature increased, thermoluminescence continued. When the temperature was permitted to drop, the luminescence ceased at a somewhat higher temperature than that at which it had started. When the temperature was again increased, luminescence started at the temperature at which it had been quenched. This cycle could be repeated many times, with a higher quenching temperature at each time. At the end of 15 minutes of luminescence, in which the temperature had gone to 145° C., the quenching temperature for sample F1 had risen from 65° to 130°. This behavior suggests the progressive emptying of more and more stable electron traps as thermoluminescence proceeds. If a sample is held at a stable temperature in this range, the luminescence declines asymptotically. The color is not noticeably affected until a temperature of about 175° is reached.

This evidence seems to indicate that thermoluminescence is caused by a mechanism that is distinct from that causing x-ray line sharpening, change of index of refraction, and the other effects related to the destruction of the purple color. The thermoluminescence is apparently caused by the infall of electrons, which begins at a temperature of about 65° C. The other changes involve destruction of the structural traps containing the electrons.

The temperatures at which thermoluminescence began are as follows:

TABLE 10. TEMPERATURE (°C.) OF BEGINNING OF THERMOLUMINESCENCE

Sample No.	Temperature (°C.)	Sample No.	Temperature (°C.)
F2	58	F3	78
F6	66	F4	65
F1	64	F5	—

These results are in essential agreement with those of Daniels and Saunders (1951), who studied thermoluminescence artificially induced in fluorite by means of cobalt 60. Using their combination furnace and photometer, they found that fluorites of various colors gave two groups of coalescing peaks: one set from 50 to 150° C., and the other set starting at 175° C. and continuing to red heat. In certain samples, only one of the sets was obtained.

None of the samples in this study fluoresced in long or short wavelength ultraviolet radiation, either before or after bleaching. All samples fluoresced blue in *x*-rays. Generally the *x*-ray fluorescence was stronger after bleaching as the sample did not absorb so much of the visible light it produced.

RE-IRRADIATION

The samples were partly recolored by exposure to unfiltered copper-target *x*-rays for 48 hours. The purple color produced was much deeper in some samples than in others. Sample F6 developed a light-purple streak in the center of the *x*-ray spectrometer sample mounting, in the course of a 20-minute spectrometer run. Sample F1 showed a barely perceptible darkening after being taped to the *x*-ray tube window for 48 hours.

The color was not stable. Forty-eight hours after the end of irradiation, all the samples had faded considerably. After a week in the dark at room temperature, the color was virtually gone.

Several of the samples were taped to the surface of a short-wavelength 15-w Sylvania mercury-vapor lamp. After 17 hours of exposure to ultraviolet radiation, no change was noted in the samples.

A cleavage fragment of yellow fluorite from southern Illinois was exposed to *x*-rays for 48 hours, then etched for 1 minute with 1:1 sulfuric acid. The etching of the purple irradiated spot was compared to that of the unexposed fluorite under the binocular microscope. No difference was observed.

Przibram (1954) describes the coloring of fluorite by alpha radiation from radium. It was possible to establish an apparently stable absorption band in the middle of the spectrum by months of exposure. Nevertheless, a certain amount of recovery took place at the red end of the spectrum; the absorption decreased gradually to the pre-irradiation level. The peak of the absorption band gradually shifts from the red end to the center of the visible spectrum as exposure continues. As it does so, it becomes less subject to this recovery effect.

Allen (1950) measured the index of refraction of fluorite prisms before and after irradiating the edge with *x*-rays for 24 hours. Although striking changes of color were readily obtained, there was no observable change in the index of refraction.

CONCLUSIONS

On being exposed to radioactivity, fluorite undergoes a number of changes in its physical properties. The fluorite turns purple. The index of refraction increases. Cracks develop and the apparent specific gravity decreases. The x-ray diffraction lines broaden and decrease in height. All of these effects, except the specific gravity change, can be reversed in an exothermic reaction that takes place at a perceptible rate above 175° C. These phenomena have a structural origin; they are apparently caused by nuclear particles disrupting the structure along their paths, after which the material recrystallized imperfectly. Raising the temperature permits the sample to recrystallize again with fewer strains and imperfections. Specimens of irradiated fluorite can be placed in a definite order of intensity of structural damage and strain, and their properties, as well as the energy released in recrystallization, vary according to this order.

The intensity of structural damage cannot be used as a method of age determination, as Hurley and Fairbairn (1953) have done with zircon. Even if it were possible to make an adequate estimate of the amount of external radioactivity, the method could show only the time since the sample cooled below 175° C. At higher temperatures, the damage was healed as quickly as it occurred.

Nor can the purple coloring be used as a geologic thermometer. It indicates that the fluorite was exposed to ionizing radiation for some time at temperatures below 175° C. But most specimens reach the observer in this condition at ordinary surface temperatures and with the radioactive material still associated with the fluorite. No geologic thermometer is needed to deduce this information.

This work was completed as part of a program conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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RELATIONSHIP OF THE MINERALS AVELINOITE, CYRILOVITE, AND WARDITE*

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Abstract

Avelinoite, the iron analogue of wardite, the isostructural aluminum compound, occurs in bright-yellow crystal aggregates in the altered zone surrounding frondelite, at the Sapucaia pegmatite mine, Minas Gerais, Brazil. Crystals are tetragonal trapezohedral (422); $a:c=1:2.650$; the forms $\{001\}$, $\{113\}$, and $\{012\}$ are present. The optical constants are: uniaxial negative, $\omega=1.803$, $\epsilon=1.769$. The measured specific gravity is 3.081 ± 0.005. The formula, $NaFe_3'''(PO_4)_2(OH)_4 \cdot 2H_2O[Z=4]$ is derived from the chemical analysis, in per cent: insoluble 1.04, Na_2O 4.70, K_2O 0.63, MnO 0.99, CaO 0.10, FeO none, Fe_2O_3 47.87, Al_2O_3 1.36, P_2O_5 29.06, H_2O 14.45; total 100.20. The space group for avelinoite, like that for wardite, is $P4_12_12$-(D_4^4,) or $P4_32_12$-(D_4^8); the cell size of avelinoite is $a_0=7.32$, $c_0=$ 19.4 Å.

Cyrilovite from West Moravia studied by the writer is identical with avelinoite; the published data for chemical composition and *d*-spacings of cyrilovite are in error, and sodium is an essential constituent of the mineral.

Introduction

In December 1954 a summary description of avelinoite, a new hydrous sodium ferric phosphate mineral from the Sapucaia pegmatite mine in Minas Gerais, Brazil, appeared in *Science* (Lindberg and Pecora, 1954), where its definitive features and isostructural relation to wardite, its aluminum counterpart, were described. In April 1955, however, a reprint came to my attention of a paper by Novotný and Staněk (1953), that described cyrilovite, a new hydrous ferric phosphate mineral from the pegmatite at Cyrilov, near Velké Mežiřiči, West Moravia. In June 1955, data for both avelinoite and cyrilovite were summarized in *Mineralogical Abstracts* (p. 512–513). The differences in the chemical analyses of the two minerals, hence the formulas derived therefrom, and the differences in *x*-ray powder-diffraction data† are very apparent; but similar cell dimensions, morphological elements, and optical constants led to a suspicion of the identity of the two. The manuscript on avelinoite was therefore delayed with the hope of procuring some type cyrilovite for laboratory examination. Through the courtesy of the late John P. Marble and George Switzer of the U. S. National Museum, specimens of cyrilovite (U. S. National Museum 107,425) were recently obtained. It is the writer's opinion that the new mineral named cyrilovite

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† Mineralogical Abstracts state that *x*-ray powder data for cyrilovite agree with goniometric results. The *x*-ray single-crystal and goniometric studies agree, but the single-crystal and powder data are inconsistent.

is inadequately described, that the published analysis, formula, and *x*-ray power-diffraction data are in error. A determination for sodium in cyrilovite by spectrographic methods shows that sodium is present in significant quantity, and, therefore, the published formula of avelinoite would apply to cyrilovite. New *x*-ray power-diffraction data for cyrilovite are consistent with the single-crystal data for cyrilovite and with the powder-diffraction data for avelinoite.

Avelinoite and cyrilovite are thus identical mineral species, isomorphous and isostructural with wardite, the sodium aluminum counterpart. There are no known intermediate member of the series, and no evidence of solid solution exists.

The name avelinoite was originally given to the mineral with formula $NaFe_3'''(PO)_2(OH)_4 \cdot 2H_2O$ in honor of Avelino Ignacio de Oliveira, eminent Brazilian geologist and Director of the National Department of Mineral Production, Rio de Janeiro.

AVELINOITE

Crystallography

Avelinoite from the Sapucaia pegmatite mine occurs in crystal aggregates together with metastrengite and leucophosphite (Lindberg, next article) in an altered zone surrounding frondelite (Lindberg, 1949). The individual crystals vary in size and are usually smaller than 0.1 mm. Many are intergrown; many others are so minute that it is not possible to measure on the goniometer faces that are observable with a high-power microscope. Crystals are squat and when single tend to lie on the basal pinacoid (Fig. 1). Morphological data for avelinoite are given in Table 1 and are there compared with data for cyrilovite. The pinacoid {001} and the dipyramid {113} are the dominant forms; all the faces of these forms tend to be present and equally well developed. The dipyramid {012} is inconspicuous and is not always present. The crystal faces are very

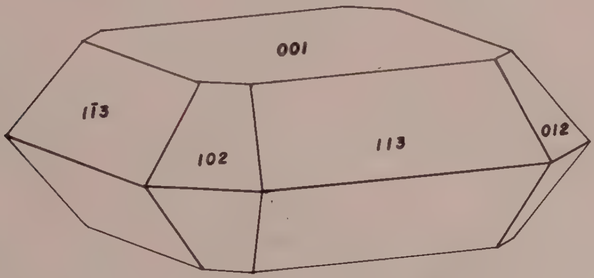

FIG. 1. Avelinoite from the Sapucaia pegmatite mine.

small and the signals observed are of poor quality; the signals observed from the form {113} are slightly better than those observed from {012}. The axial ratio, as calculated from the single-crystal x-ray measurements, $a_0:c_0=1:2.650$ is considered more accurate than that which may be derived from the measured ρ for the forms {012} and {113}; the range in measured ρ varies $3\frac{1}{2}$° for {012} and 5° for {113}.

TABLE 1. MORPHOLOGICAL DATA FOR AVELINOITE AND CYRILOVITE
Crystal class: Tetragonal trapezohedral (422)

Avelinoite $a:c=1:2.650$; $p_0:r_0=2.650:1$						Cyrilovite[1] $a:c=1:2.650$; $p_0:r_0=2.650:1$			
Form	Number of observations	ρ measured		ϕ Calculated	ρ Calculated	Form	ρ Measured	ϕ Calculated	ρ Calculated
		Range	Mean						
001	6				0°00′	001			0°00′
012	10	52°00′–55°25′	53°33′	0°00′	52°58′	012	53°50′	0°00′	52°59′
113	18	48°20′–53°00′	50°35′	45°00′	51°20′	110	90°20′	45°00′	90°00′
						114	43°03′	45°00′	43°03′
						55·12	57°41′	45°00′	57°18′

[1] Data of Novotný and Staněk (1953). In the original measurements crystals of cyrilovite were oriented with ϕ at 45° to the orientation of the primitive cell; the forms given here have been re-oriented in the direction of the primitive cell, using the true c-axis, which is twice the length of the morphologically determined c-axis. Equivalent forms in both orientations will have equal ρ values; ϕ values will be at 45°00′.

The crystal class for both avelinoite and for wardite is tetragonal trapezohedral (422). The crystal forms observed on both avelinoite and wardite are consistent with this crystal class. Hurlbut (1952) noted that the wardite crystals from Beryl Mountain, New Hampshire, have higher symmetry than that required by the tetragonal pyramidal class (4), to which class wardite had been previously assigned.

Physical properties

Avelinoite is orange to brownish yellow. The powder is yellow.

The specific gravity, as measured on the sample used for analysis by means of an Adams-Johnston pycnometer of fused silica, is 3.081 ± 0.005. That calculated from x-ray data is 3.09 for the avelinoite end member, and 3.07 for avelinoite containing 4 per cent of the wardite component assuming the same volume for each. Since chemical analysis shows substitution not only of Al for Fe, but also of K and Mn for Na, measured and observed specific gravities are considered to be in good agreement. Avelinoite is uniaxial negative with $\omega=1.803$ and $\epsilon=1.769$. The absorption is deep yellow with $O \geqq E$. The small size of the crystals made determination of the hardness impracticable.

Chemical properties

Avelinoite is a hydrous sodium iron phosphate with a simplified formula corresponding to $NaFe_3'''(PO_4)_2(OH)_4 \cdot 2H_2O$. Chemical analysis (Table 2) shows substitution of K for Na and Al for Fe. The role of manganese is uncertain. It may occur in avelinoite as a substitution for sodium, or as a surface staining of unknown nature, or as an impurity from admixed frondelite. Frondelite, $Mn''Fe_4'''(PO_4)_3(OH)_5$, occurs in the analyzed sample of avelinoite, both as very fine discrete grains and as small residual fibers in the core of avelinoite crystals. Subtraction of small quantities of frondelite from the analysis of avelinoite affects the ratios derived from avelinoite such that (1) the ratios for alkali,

TABLE 2. CHEMICAL ANALYSES OF AVELINOITE AND CYRILOVITE

	Theoretical composition	Cyrilovite[1]	Avelinoite[2]	Recalculated to 100% without insoluble	Ratios	Oxygen equivalents[3]	Metal equivalents	Metal atoms in unit cell[3]
Insoluble			1.04					
Na_2O	6.40		4.70	4.74	0.0765	0.0765	0.1529	2.97
K_2O			0.63	0.64	0.0068	0.0068	0.0136	0.26
MnO			0.99	1.00	0.0141	0.0141	0.0141	0.27
CaO			0.10	0.10	0.0018	0.0018	0.0018	0.03
FeO			None	None				
Fe_2O_3	49.43	50.89	47.87	48.28	0.3023	0.9069	0.6046	11.72
Al_2O_3			1.36	1.37	0.0134	0.0403	0.0268	0.52
P_2O_5	29.30	33.96	29.06	29.30	0.2064	1.0320	0.4128	8.00
H_2O	14.87	15.14	14.45	14.57	0.8087	0.8087	1.6174	31.38
Total	100.00	99.99	100.20			2.8871		
Sp. gr.		3.085	3.081					

[1] Analysis of Novotný and Staněk (1953). Spectrographic analysis, in per cent, U. S. National Museum 107,425, by Harry Bastron, U. S. Geological Survey, gives in addition 0.3 Mn; 1.4 Al, 0.2 Sc, 1.2 Ti, 0.04 Zr, 0.2 Mg; 0.6 Ca, 0.06 Sr, 0.004 Ba, 4 Na, X Si; 4 Na is equivalent to 5.4 per cent Na_2O.

[2] M. L. Lindberg, Analyst. Cell constants: $Na_4Fe_{12}'''(PO_4)_8(OH)_{16} \cdot 8H_2O$. Actual ratios $(Na_{2.97}K_{0.26}Mn_{0.27}Ca_{0.03})(Fe_{11.72}'''Al_{.52})(PO_4)_8(OH)_{15.38} \cdot 8H_2O$. The insoluble consists of quartz. Spectrographic analysis, in per cent, by Janet Fletcher of the U. S. Geological Survey shows in addition 0.0X Mg, Ti, Be; 0.00X Ba; 0.000X Sr.

[3] On basis of 56 oxygen atoms per cell.

water, and trivalent ions more closely approach theoretical values, (2) the ratio of phosphate ion is slightly lowered, and (3) the amount of manganese is lowered in proportion to the amount of frondelite subtracted. If all the manganese present is from frondelite, a maximum impurity of 11 per cent of frondelite would be present in the analyzed powder of avelinoite. Grain counts indicate approximately 4 per cent frondelite, plus a much smaller amount of surface staining of unknown nature.

Avelinoite is soluble in hot dilute HCl, in hot dilute H_2SO_4, and, with difficulty, in hot dilute HNO_3. In the closed tube, it gives off water and fuses.

X-ray Data

Single-crystal rotation and Weissenberg pictures about the *a*- and *c*-axes of avelinoite indicate a mineral of tetragonal symmetry with the following reflections present: ($hk0$), ($h0l$), and (hkl) all orders; ($h00$), $h=2n$; ($00l$), $l=4n$. These reflections are identical with those recorded by Larsen (1942, p. 292) for wardite, the isostructural aluminum mineral. The space group for both avelinoite and for wardite as determined from these reflections is $P4_12_12$-(D_4^4) or $P4_32_12$-(D_4^8), not $P4_1$-(C_4^2) as previously recorded. The new space group is in the tetragonal trapezohedral class (422). The symmetry of the measured crystals is consistent

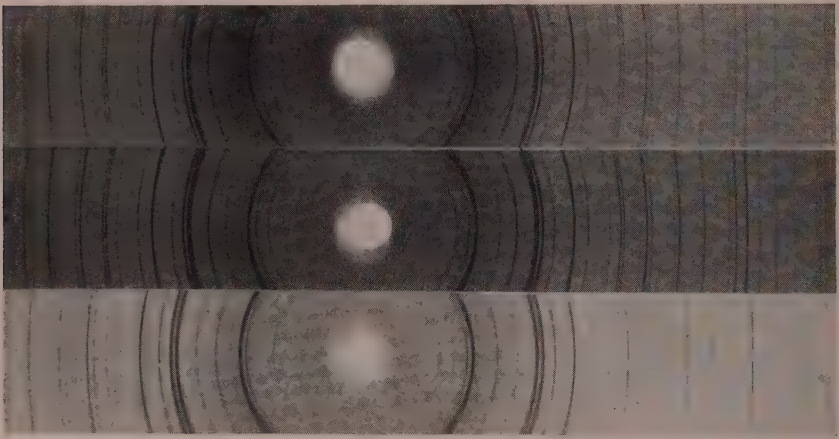

Plate 1. Powder diffraction patterns of cyrilovite, avelinoite, and wardite. (1) Cyrilovite, Cyrilov, Velké Mežiřiči, West Moravia; U. S. National Museum 107,425; iron radiation, manganese filter. (2) Avelinoite, Sapucaia pegmatite, Brazil; iron radiation, manganese filter. (3) Wardite, Beryl Mountain, New Hampshire; iron radiation, manganese filter; center of film offset in relation to avelinoite to emphasize difference in cell size.

TABLE 3. *X*-RAY DIFFRACTION DATA FOR AVELINOITE, CYRILOVITE, AND WARDITE

Single-Crystal Data

Avelinoite	Cyrilovite[1]	Wardite[2]
$a_0=7.32$, $c_0=19.40$ Å	$a_0=7.32$, $c_0=19.4$ Å	$a_0=7.04$, $c_0=18.88$ Å
$a:c=1:2.650$	$a:c=1:2.650$	$a:c=1:2.6818$
volume = 1040 Å^3		
cell weight = 1930		
cell contents:		
$Na_4F_{12}(PO_4)_8(OH)_{16}\cdot 8H_2O$		$Na_4Al_{12}(PO_4)_8(OH)_{16}\cdot 8H_2O$
Sp. gr. = 3.081 ± 0.005 (measured)		2.81 (meas.)
Sp. gr. = 3.09 (calculated)		2.81 (calc.)

Powder Diffraction Data

Avelinoite[3]				Cyrilovite[4]		Cyrilovite[5]			Wardite[6]		
I	d (Å) meas.	Index	d (Å) calc.	I	d (Å) meas.	I	d (Å) meas.	sin θ	I	d (Å) meas.	Index
½	6.87	101	6.85	½	6.83				2	6.63	101
3	5.85	102	5.84	3	5.85	VW	5.50	0.1627	2	5.68	102
3	5.19	110	5.18	2	5.19	M	5.04	0.1774	3	4.99	110
10	4.85	004	4.85	10	4.85	VS	4.64	0.1927	10	4.74	004
		103	4.85								103
1	4.56	112	4.57						1	4.42	112
3	4.05	104	4.04	2	4.05	VW	3.89	0.2297	3	3.94	104
		113	4.04								113
½	3.65	200	3.66								
5	3.60	201	3.60	4	3.60	M	3.53	0.2536	2	3.47	201
½	3.31	210	3.27								
3	3.230	211	3.228	2	3.226	M	3.16	0.2829	3	3.110	211
8	3.186	203	3.186	8	3.186	M	3.02	0.2963	6	3.085	203
7	3.101	115	3.105	5	3.101	W	2.862	0.3125	2	3.025	115
		212	3.102						7	2.994	212
3	2.913	204	2.921	3	2.920	?	2.623	0.3410	4	2.825	213
		213	2.920						1	2.629	214
8	2.658	205	2.663	8	2.664	?	2.519	0.3551	7	2.591	205
3	2.502	215	2.502	3	2.505	W	2.445	0.3657	2	2.539	107
		222	2.501						1	2.388	117, 008
2	2.296	108	2.302	2	2.301	W	2.252	0.3971	2	2.256	108
3	2.210	207	2.209	3	2.207	S	2.179	0.4105	2	2.156	207
3	2.182	304	2.181	3	2.180	?	2.144	0.4171	4	2.108	
		313	2.180						1	2.063	
½	2.156	225	2.154	½	2.156				1	2.027	
½	2.116	217	2.116	½	2.116				1	2.004	
1	2.067	109	2.067	1	2.067				2	1.961	
		305	2.066						2	1.926	
4	2.020	226	2.021	4	2.020	M	1.989	0.4496	1	1.827	
		321	2.019						½	1.841	
2	1.990	315	1.988	2	1.990	?	1.962	0.4558	1	1.815	
½	1.943	306	1.948	½	1.943				4	1.764	
½	1.875	10.10	1.876	½	1.871				½	1.674	
1	1.854	209	1.857	½	1.854				½	1.666	
4	1.833	307	1.832	3	1.833	M	1.807	.04949	1	1.656	
		400	1.830						1	1.639	
3	1.714			2	1.718	M	1.694	0.5280	1	1.590	
½	1.668			½	1.664				½	1.573	
½	1.658			½	1.654	?	1.646	0.5434	½	1.559	

TABLE 3—(*continued*)

Powder Diffraction Data

Avelinoite[3]				Cyrilovite[4]		Cyrilovite[5]			Wardite[6]		
I	d (Å) meas.	Index	d (Å) calc.	I	d (Å) meas.	I	d (Å) meas.	sin θ	I	d (Å) meas.	Index
1	1.638			½	1.634				2	1.534	
1	1.615			1	1.615	?	1.601	0.5587	5	1.516	
3	1.589			3	1.589	W	1.570	0.5826	2	1.460	
5	1.553			4	1.553	VS	1.535	0.5980	½	1.426	
2	1.510			2	1.510	W	1.496	0.6182	½	1.422	
2	1.462			2	1.462	W	1.447	0.6324	½	1.399	
1	1.450			½	1.450				1	1.392	
1	1.434			½	1.432	W	1.414	0.6324	½	1.386	
1	1.411			½	1.411	W	1.395	0.6413	½	1.381	
½	1.403			½	1.403				2	1.368	
1	1.380			½	1.380				1	1.356	
2	1.357			1	1.358				2	1.333	
2	1.349			1	1.349	M	1.337	0.6690	1	1.319	
½	1.332								1	1.300	
½	1.306								½	1.284	
3	1.296			2	1.296	M	1.284	0.6965	½	1.272	
½	1.284								½	1.268	
½	1.271								½	1.255	
3	1.254			2	1.253	M	1.240	0.7211	½	1.250	
1	1.234								½	1.216	
1	1.218			½	1.218	W	1.209	0.7398	1	1.197	
½	1.211								1	1.175	
½	1.202			½	1.202	W	1.191	0.7509	1	1.142	
½	1.196			½	1.195	VW	1.180	0.7579	½	1.087	
1	1.184			½	1.184	?	1.159	0.7718	½	1.081	
½	1.165			½	1.164	VW	1.147	0.7800	½	1.074	
½	1.152			½	1.151	VW	1.138	0.7860	½	1.055	
½	1.150								½	1.051	
1	1.142			1	1.142	?	1.133	0.7898	½	1.031	
½	1.127			½	1.127	?	1.128	0.7929	1	1.017	
½	1.103			½	1.102	W	1.019	0.8774	1	1.004	
½	1.087								½	0.9965	
½	1.056								2	0.9897	
½	1.044										
½	1.034										
½	1.021										
2	1.013			1	1.014	M	1.009	0.8861			
1	1.004					?	.9993	0.8951			
3	0.9940			2	.9938	S	.9908	0.9028			
						M	.9803	0.9124			
2	0.9843			1	.9822	M	.9657	0.9262			

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[1] Cyrilovite, Cyrilov, Velké Meźiřiči, West Morovia. Data of Němec (Novotný and Staněk, 1953).

[2] Wardite, Beryl Mountain, N. H. Data of Hurlbut (1952).

[3] Avelinoite, Sapuacia Pegmatite. Iron radiation, manganese filter Debye-Sherrer camera diameter 114.59 mm.

[4] Cyrilovite, U.S.N.M. 107,425; Cyrilov, Velké Meźiřiči, West Moravia. Iron radiation, manganèse filter Debye-Sherrer camera diameter 114.59 mm. Data of Lindberg.

[5] Cyrilovite (same locality); values of sin θ from Table 2 of type description (Novotný and Staněk, 1953) transformed to d-spacings by Lindberg, using $K\alpha = 1.7889$, cobalt radiation. Sin $\theta = 0.2963$ was substituted for sin $\theta = 0.2987$ to conform with $\theta = 17°14'$.

[6] Wardite, Beryl Mtn., N. H., Harvard No. 103,379. Iron radiation, manganese filter Debye-Sherrer camera diameter 114.59 mm.

with this class. Donnay (1954, p. 380) corrected the space group of wardite to be consistent with reflections listed by Larsen, but did not change the crystal class C_4^2 (p. 40) to D_4^4 or D_4^8 (p. 46), as noted by Heritsch (1955, p. 249).

The cell dimensions and powder diffraction data for avelinoite, cyrilovite, and wardite are given in Table 3. The indexing of planes of high *d*-spacing in avelinoite is on the basis of reflections also observed in the single-crystal studies; planes with low *d*-spacing have not been indexed because of the large number of possible choices. Calculated *d*-spacings for comparable reflections in wardite will be given in a later paper by Lindberg describing the relationship of millisite to the wardite-avelinoite (cyrilovite) series. The isostructural relationship and differences in cell size of avelinoite and of wardite are illustrated in Plate 1, where their powder-diffraction patterns are compared.

CYRILOVITE

In 1953 Novotný and Staněk published a description of a new mineral, cyrilovite. This mineral now appears, by re-examination by the present author of type material (U. S. National Museum 107,425), to be the same species as avelinoite although the original data of cyrilovite were only in partial agreement with the data for avelinoite. The chemical composition, formula, and *x*-ray powder-diffraction data for cyrilovite cited in the original paper are inconsistent with data for avelinoite and the identity of the two minerals cannot be established from published data alone.

Crystals of both cyrilovite and avelinoite are tetragonal; the direction for the *a*-axis selected by Novtný and Staněk (1953) is at a 45° angle to the smallest primitive unit cell for cyrilovite and also at 45° to the direction selected by Lindberg for avelinoite. After adjustment for this difference in orientation and doubling of the *c*-axis, the $a:c$ ratio of both minerals is the same. The forms given by Novotný and Staněk for cyrilovite become in the primitive lattice $\{001\}$ the same, $\{010\}=\{110\}$, $\{111\}=\{012\}$, $\{011\}=\{114\}$, $\{053\}=\{55.12\}$.

The optical properties for cyrilovite are $\omega=1.805$, $\epsilon=1.777$ (Novotný and Staněk, 1953). The measured specific gravity of cyrilovite is 3.085 (Novotný and Staněk) compared with 3.081 ± 0.005 for avelinoite.

The chemical analysis of cyrilovite, as determined upon a sample weighing 0.018 gram (Novotný and Staněk, 1953), is recorded in Table 2 where it may be compared with the analysis of avelinoite. Sodium was recorded in spectrographic traces only. Harry Bastron of the U. S. Geological Survey re-examined cyrilovite (U. S. National Museum 107,425) spectrographically and reports approximately 4 per cent Na which is equivalent to 5 per cent Na_2O, indicating that sodium is an essential component in cyrilovite; the published analysis of the other components, which total 99.99 per cent without considering the sodium content, is in error. The published analysis of cyrilovite cannot therefore be used to determine the correct formula for cyrilovite.

The cell dimensions of cyrilovite obtained from single-crystal studies as determined by Němec (Novotný and Staněk, 1953, p. 334) agree exactly with those of avelinoite; cyrilovite, tetragonal, $c_0=19.4$, $a_0=7.32$ Å; avelinoite, tetragonal, $c_0=19.4$, $a_0=7.32$ Å; however, the *x*-ray powder-diffraction data for cyrilovite, obtained by Černohorský (Novotný and Staněk, 1953, p. 329) are not in agreement with the data for avelinoite. A comparison of the powder diffraction data for the two minerals (Table 3) shows:

1. The powder pattern of avelinoite may be indexed using the values of a_0 and c_0 derived from single-crystal data.
2. The powder pattern of cyrilovite (original data) cannot be indexed by using the values of a_0 and c_0 derived from single crystal data.
3. To the extent that the intensities of reflections are indicated, the succession of strong and weak lines for cyrilovite is not the same as for avelinoite, and entirely different reflections would be used in cataloging for identification.

In order to investigate the discrepancies in the powder data for cyrilovite, as compared with avelinoite and with the single crystal data, an *x*-ray powder-diffraction pattern of type material (U. S. National Museum 107,425) was taken (pl. 1). The *d*-spacings and their relative intensities so obtained (Table 3) are consistent with those of avelinoite and indicate that there is a fundamental error in the published data for cyrilovite. The *d*-spacings obtained by Černohorský (data, Table 3, transformed from sin θ by the present author) are too small for the cell size and indicate a cell size smaller than that of wardite, the isostructural aluminum compound. That significant differences in cell size for avelinoite and wardite exist is illustrated in Plate 1; reflections aligned on the right of center are considerably offset to the left of center.

CONCLUSIONS

Avelinoite and cyrilovite are believed to be the same mineral species. The published description of cyrilovite only suggests the possibility of identity of the two minerals. Examination of type material of cyrilovite established the presence of sodium in cyrilovite in quantity sufficient to enter the formula. The published formula of avelinoite may be applied to cyrilovite. The new formula and the corrected *x*-ray powder data for cyrilovite, which make the powder and single-crystal data consistent, also permit the relationship of cyrilovite to wardite to be recognized.

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LEUCOPHOSPHITE FROM THE SAPUCAIA PEGMATITE MINE, MINAS GERAIS, BRAZIL*

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ABSTRACT

At the Sapucaia pegmatite mine, Minas Gerais, Brazil, leucophosphite [$KFe_2'''(PO_4)_2(OH)\cdot 2H_2O$] occurs sparingly as minute buff-colored crystals in vugs in frondelite. The optical constants are $\alpha=1.707$, $\beta=1.721$, and $\gamma=1.739$; biaxial positive; dispersion $v>r$ very strong. Leucophosphite is monoclinic, pseudo-orthorhombic, space group $P2_1/n$ (primitive cell); the cell dimensions are $a_0=9.73$, $b_0=9.60$, and $c_0=9.69$ Å; $\beta=102°16'$; the principal d-spacings occur at 6.79, 5.99, and 3.061 Å. The chemical analysis, in per cent, is K_2O 10.93, Na_2O 0.53, Fe_2O_3 41.02, Al_2O_3 0.25, Mn_2O_3 0.57, P_2O_5 34.71, H_2O 11.20, insoluble matter 0.45; total 99.66.

INTRODUCTION

This paper presents a detailed mineralogical description of leucophosphite, $KFe_2'''(PO_4)_2(OH)\cdot 2H_2O$, from the Sapucaia pegmatite mine, Minas Gerais, Brazil. Leucophosphite has previously been reported only from two deposits, both of sedimentary origin: (1) from Weelhamby Lake, Nighanboun Hills, Western Australia (Simpson, 1931–32), where it occurs as fine-grained chalklike masses which derive their phosphate content from bird guano; and (2) from Bomi Hill, Western Liberia (Axelrod et al., 1952) where it occurs in heterogeneous metacolloidal masses which derive their phosphate content from bat dung. The leucophosphite from the Sapucaia pegmatite mine represents not only the first known occurrence of leucophosphite in a pegmatite but also the first natural occurrence in well-defined crystals. Synthetic crystals (Haseman, Lehr, and Smith, 1950) have been prepared at temperatures ranging between 75° and 145° C., at a pH of 2.5 to 6.0, and at phosphate concentrations from 1.0 to 3.5M.

The Sapucaia pegmatite mine is in the municipality of Galilea in the Rio Doce valley region of eastern Minas Gerais. This mine was mapped and a suite of minerals collected by W. T. Pecora and A. L. de M. Barbosa during the years 1942–45. Minerals already described from this pegmatite include frondelite (Lindberg, 1949), faheyite (Lindberg and Murata, 1953), moraesite (Lindberg, Pecora, and Barbosa, 1953), tavorite and barbosalite (Lindberg and Pecora, 1954*a*), and avelinoite (Lindberg and Pecora, 1954*b*). The mica deposits and general features of the pegmatite have been described by Pecora and others (1950).

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* Publication authorized by the Director, U. S. Geological Survey.

OCCURRENCE

Leucophosphite occurs sparingly in close association with avelinoite† and metastrengite in crystal aggregates that line vugs in frondelite. The material replacing the frondelite walls of the vugs is crudely layered. Metastrengite is most abundant on the outside of the specimens where it occurs interstitially to compact masses of radiating fibers of frondelite. The frondelite is partly altered and the masses of fibers may form a loose meshwork interstitial to which grow crusts of crystals of avelinoite, together with minor amounts of leucophosphite. The leucophosphite crystals frequently contain a few radiating fibers of residual frondelite.

Metastrengite, $FePO_4 \cdot 2H_2O$, avelinoite, $NaFe_3'''(PO_4)_2(OH)_4 \cdot 2H_2O$, and leucophosphite, $KFe_2'''(PO_4)_2(OH) \cdot 2H_2O$ are secondary minerals after frondelite, $MnFe_4'''(PO_4)_3(OH)_5$. Frondelite contains a small amount of sodium (Na_2O 0.98 per cent) and potassium (K_2O 0.12 per cent), probably substituting for manganese. Although all the chemical constituents are present in frondelite for the formation of the secondary minerals metastrengite, avelinoite, and leucophosphite, it seems likely that sodium and potassium solutions reacted with frondelite to form avelinoite and leucophosphite. The space occupied by vugs in the frondelite is insufficient to yield, through leaching of frondelite, enough sodium and potassium to form masses of avelinoite and leucophosphite.

CRYSTALLOGRAPHY

Leucophosphite occurs in minute doubly terminated diamond-shaped plates (Fig. 1). The habit and morphological measurements suggest a holohedral orthorhombic mineral. Single-crystal Weissenberg photographs by their intensity distribution and lattice level symmetry show that leucophosphite is actually monoclinic. The extinctions observed on the Weissenberg patterns are consistent with the space group $P2_1/n(C_{2h}^5)$ and the habit of the crystals confirm a center of symmetry.

The crystallographic elements for both the primitive monoclinic and for the pseudo-orthorhombic *B*-centered settings are given in Table 1. Goniometric measurements were made on eight crystals oriented parallel to the *c*-axis, and on three crystals oriented parallel to the *a*-axis, pseudo-orthorhombic *B*-centered setting. Calculated differences in ϕ and ρ angles between ± forms (elements calculated from *x*-ray data) are smaller than the error of measurement on the two-circle goniometer. For this reason the choice of (111) and ($\bar{1}11$) (morphological data, Table 1) has been made on a statistical basis—that is, data for the pair of faces symmetrical to the *ac* symmetry plane with the largest values of ϕ and ρ are

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† See preceding article.

TABLE 1. MORPHOLOGICAL DATA[1]

(measured)

Forms	ϕ Range	ϕ Average	ρ Range	ρ Average	A[2] Range	A Average
100	—	90°00′	89°20′–92°30′	90°25′	—	0°00′
210	51°50′–52°37′	52°02′	89°36′–91°02′	90°21′	—	—
111	32°37′–34°08′	33°08′	57°30′–59°08′	57°54′	62°00′–63°43′	62°52′
$\bar{1}11$	−31°30′–32°46′	32°05′	55°22′–58°00′	57°07′	63°00′–64°32′	63°33′

CRYSTALLOGRAPHIC ELEMENTS AND ANGLE TABLE

(calculated from x-ray data)

Pseudo-orthorhombic orientation

Monoclinic; prismatic $2/m$ Space group: $B2_1/n$ (C_{2h}^5)

$a:b:c=1.577:1:1.267$; $\beta=90°12'$; $p_0:q_0:r_0=0.8035:1.267:1$
$r_2:p_2:q_2=0.7893:0.6342:1$; $\mu=89°48'$; p_0' 0.8035, q_0' 1.267, x_0' 0.0035

Forms	ϕ	ρ	ϕ_2	$\rho_2=B$	C	A
100	90°00′	90°00′	0°00′	90°00′	89°48′	0°00′
210	51°45′	90°00′	0°00′	51°45′	89°51′	38°15′
111	32°30′	56°21′	51°05′	45°24′	56°15′	63°26′
$\bar{1}11$	−32°16′	56°16′	128°38′	45°18′	56°23′	116°21′

Primitive orientation

Monoclinic; prismatic—$2/m$ Space group: $P2_1/n$ (C_{2h}^5)

$a:b:c=1.013:1:1.009$; $\beta=102°16'$; $p_0:q_0:r_0=0.996:0.986:1$
$r_2:p_2:q_2=1.014:1.010.1$; $\mu=77°44'$; p_0' 1.109, q_0' 1.009, x_0' 0.2174

Forms	ϕ	ρ	ϕ_2	$\rho_2=B$	C	A
110[3]	45°18′	90°00′	0°00′	45°18′	81°19′	44°42′
011	12°10′	45°53′	77°44′	45°25′	44°35′	81°19′
$\bar{1}01$	90°00′	38°43′	128°43′	90°00′	50°59′	128°43′
$\bar{1}11$	−38°28′	52°11′	128°43′	51°48′	60°21′	119°26′

---

[1] Pseudo-orthorhombic orientation was used in measuring these crystals.

[2] Three crystals were measured in a position with (100) polar.

[3] Equivalent forms:

B-centered orientation	Primitive orientation
100	$\bar{1}01$
210	$\bar{1}11$
111	011
$\bar{1}11$	110

tabulated as (111); data for the other pair of faces are tabulated ($\bar{1}11$). Measured values of ϕ and ρ are considered only as indicative of which forms are present; the crystallographic elements and angle table have been calculated from the x-ray data which are considered more accurate.

The unit-cell dimensions as derived from rotation and Weissenberg photographs subsequently adjusted to measurements on a shrinkage-corrected powder photograph are $a_0=9.73$, $b_0=9.60$, $c_0=9.69$ Å., all ± 0.04 Å, $\beta=102°16'\pm 15'$, primitive monoclinic cell, and $a_0=15.14$, $b_0=9.60$, and $c_0=12.16$ Å, $\beta=90°12'\pm 15'$, pseudo-orthorhombic B-centered cell. The measured d-spacings on the Weissenberg photograph for $h0l$ and $h0\bar{l}$ establish unequivocally the position of the obtuse angle β in the B-centered orientation, even though β values of $90°12'\pm 15'$ may imply no choice in the position of the obtuse angle. The transformation matrix, pseudo-orthorhombic cell to the primitive cell, is $\bar{\frac{1}{2}}0\frac{1}{2}/010/\frac{1}{2}0\frac{1}{2}$ and for primitive to pseudo-orthorhombic is $\bar{1}01/010/101$. D-spacings have been calculated for all indices possible in the space group $P2_1/n$ for values of h, k, and $l=0$, 1, 2, and 3. Those consistent with the

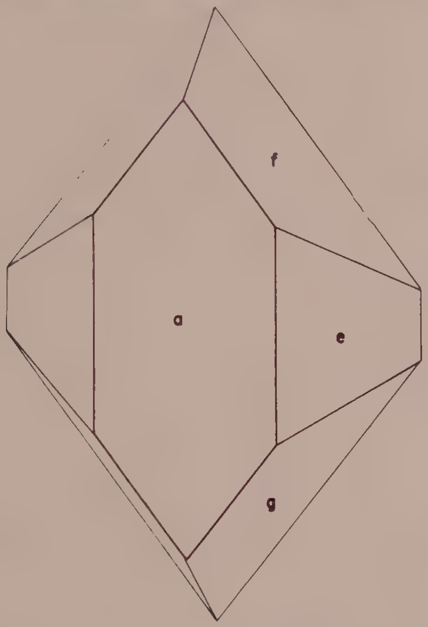

FIG. 1. Leucophosphite

	a	*e*	*f*	*g*
B-centered Forms	100	210	111	111
Primitive Forms	$\bar{1}01$	$\bar{1}11$	011	110

measured *d*-spacings are given in Table 2. The close agreement of axial lengths yields a multiple choice of indices in the comparison of calculated and measured *d*-spacings as values of *h*, *k*, and *l* are transposed. It is known from single-crystal Weissenberg data that the intensity of reflections with *d*-spacings of the same order of magnitude varies considerably. In the powder pattern weak reflections may enhance the intensity of strong reflections, or, if resolved, may not appear. The minimum difference in 2θ between reflections not resolved and those resolved has not been evaluated. Indices for reflections are therefore considered as tentative.

PHYSICAL PROPERTIES

Leucophosphite is buff-colored. It has an excellent cleavage parallel to (100) (pseudo-orthorhombic orientation). The specific gravity, as measured on the sample used for analysis by means of an Adams-Johnston pycnometer of fused silica, is 2.948. The specific gravity calculated from *x*-ray data for the end member without substitution by sodium or aluminum is 2.957. The small size of the crystals made determination of the hardness impracticable.

Leucophosphite from the Sapucaia pegmatite is biaxial (+), with indices of refraction $\alpha=1.707$, $\beta=1.721$, and $\gamma=1.739$ (all ± 0.002). The calculated 2V is 84°. The dispersion is $v>r$, very strong. The optical orientation (pseudo-orthorhombic axes) is $X=b$, $Z\wedge c=26°$. The sense of $Z\wedge c(+$ cr $-)$ has not been determined because the acute and obtuse angles ($\beta=90°12'$) were not differentiated during the microscopic examination. The optical data for the synthetic crystals (Haseman et al., 1950, p. 82) are $\alpha=1.706$, $\beta=1.720$, $\gamma=1.741$; biaxial (+); $2V=81°$; $\beta=102°$; $r>v$. The dispersion formula for the naturally occurring and for the synthetic crystals is reversed.

The extinction angles of Lindberg ($Z\wedge c=26°$) and Haseman ($Z\wedge c=30°$) seem consistent, but the choice of the *c*-direction by the two authors may not be identical, since the $Z\wedge c$ given by Lindberg refers to the *B*-centered orientation and the monoclinic β angle of Haseman is equivalent to the β angle of the primitive cell of Lindberg.

CHEMICAL PROPERTIES

Leucophosphite is a hydrous potassium iron phosphate with formula $KFe_2'''(PO_4)_2(OH)\cdot 2H_2O$. The analysis (Table 3) is in agreement with the theoretical composition of the synthetic compound (Haseman et al., 1950). It differs greatly from the analyses of the leucophosphite from the two occurrences of sedimentary origin, both samples of which contain known mineral impurities, in addition to which the samples themselves

TABLE 2. *X*-RAY POWDER DIFFRACTION DATA FOR LEUCOPHOSPHITE FROM THE SAPUCAIA PEGMATITE MINE AND FOR SYNTHETIC LEUCOPHOSPHITE

Sapucaia[1]		Synthetic[2]		Possible indices, primitive monoclinic lattice							
I	$d_{meas.}$	*I*	$d_{meas.}$	*hkl*	$d_{calc.}$	*hkl*	$d_{calc.}$	*hkl*	$d_{calc.}$	*hkl*	$d_{calc.}$
3	7.60 Å	.31	7.50	$10\bar{1}$	7.57 Å						
10	6.79	1.00	6.77	110	6.76						
1	6.09	—	—	101	6.09						
7	5.99	.76	5.92	$11\bar{1}$	5.94						
3	4.76	.28	4.73	020	4.80	200	4.76	002	4.74		
2	4.28	.21	4.23	120	4.28	021	4.28	210	4.26	012	4.25
2	4.21	.28	4.20	$21\bar{1}$	4.20	112	4.19				
2	4.08	.14	4.05	$12\bar{1}$	4.05						
3	3.79	.21	3.78	$20\bar{2}$	3.79	121	3.77				
1	3.65	—	—	211	3.63	112	3.63				
1	3.54	—	—	$21\bar{2}$	3.52						
3 B	3.37	.35	3.34	220	3.38	022	3.37	$22\bar{1}$	3.35	$12\bar{2}$	3.34
½	3.25	.14	3.20	$30\bar{1}$	3.22						
½	3.23	.14	3.09	$10\bar{3}$	3.20						
7	3.06	.59	3.03	$31\bar{1}$	3.05	$11\bar{3}$	3.04	202	3.04		
				211	3.04	122	3.03	130	3.03	031	3.03
1	3.017	.28	3.00	310	3.010	013	2.998				
1	2.990	.28	2.97	$22\bar{2}$	2.973						
1	2.956	—	—	$13\bar{1}$	2.948						
4	2.916	.37	2.90	212	2.903						
4	2.829	.41	2.81	131	2.833	301	2.828	103	2.820		
1	2.685	.35	2.66	$32\bar{1}$	2.675	$12\bar{3}$	2.667				
3	2.655	.37	2.64	230	2.655	032	2.652	320	2.645	023	2.637
1	2.586			222	2.570						
1	2.542	.17	2.53	$30\bar{3}$	2.523						
1	2.484	.17	2.48								
1	2.451										
½	2.412										
1	2.384	.17	2.38								
2	2.345	.21	2.33								
½	2.323										
½	2.220										
1	2.179										
1	2.154	.21	2.14								
½	2.091										
½	2.041										
1 B	1.998										
½	1.972										
½	1.960										
1 B	1.926										
1	1.899										
2	1.823										
1	1.786										
½	1.754										
½	1.709										
½	1.701										
1 B	1.687										
½	1.660										
½	1.653										
½	1.617										
½	1.602										
1	1.584										
1	1.570										
½	1.525										
½	1.512										
½	1.501										
½	1.490										
½	1.460										
½	1.452										
½	1.432										
½	1.403										
½ B	1.377										
½	1.360										
½	1.348										
½	1.337										
½	1.327										
½	1.313										

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[1] Iron radiation $FeK\alpha = 1.9373$, Debye-Sherrer camera, diameter 114.59 mm. Film shrinkage negligible; values of $2\theta \pm 0.1°$ for lines intensity $> \frac{1}{2}$; $\pm 0.2°$ for broad lines (B) and lines of intensity $= \frac{1}{2}$. Indices are considered as tentative and intensity contribution and resolution of the several suggested indices have not been evaluated.

[2] Data from Haseman and others (1950).

are heterogeneous, showing a varied degree of crystallinity to *x*-rays, from amorphous to well crystallized. The amorphous material cannot be strictly identified with the crystalline leucophosphite as described in this paper and can be expected to show some variation in composition.

Leucophosphite is soluble in hot dilute HCl (1:1) and H_2SO_4 (1:1). When heated in the closed tube it gives off water.

TABLE 3. CHEMICAL ANALYSIS OF LEUCOPHOSPHITE

	(1)	(2)	(3)	(4)	(5)	(6)	Ratios	Metal equivalent	Oxygen equivalent	Metal atoms in unit cell*
K_2O	7.86	7.88	12.2	11.96	10.93	11.02	0.1170	0.2340	0.1170	3.71
Na_2O	0.22	0.13			0.53	0.53	0.0056	0.0112	0.0056	0.18
$(NH_4)_2O$	1.99	0.09								
FeO	0.14	0.00			none					
CaO	0.16	trace								
MgO	0.02	0.73								
MnO		0.22								
Fe_2O_3	36.85	32.82	38.9	40.55	41.02	41.35	0.2589	0.5178	0.7767	8.20
Al_2O_3	0.88	12.73			0.25	0.25	0.0024	0.0048	0.0072	0.07
Mn_2O_3					0.57	0.57	0.0036	0.0072	0.0108	0.11
TiO_2	0.41									
P_2O_5	33.46	26.69	37.4	36.07	34.71	34.99	0.2465	0.4930	1.2325	7.81
CO_2		0.17								
$C_{organic}$	0.30	trace								
H_2O^+	11.67	12.28			11.20	11.29	0.6267	1.2534	0.6267	9.86
H_2O^-	1.23	6.59								
Ignition loss			11.6	11.42						
Insoluble	(4.92)				0.45					
SiO_2	4.32									
Total	99.51	100.33	100.1	100.00	99.66	100.00			2.7765	

(1) Leucophosphite, Bomi Hill, Liberia, M. K. Carron, analyst (Axelrod et al., 1952).
(2) Leucophosphite, Ninghanboun Hills, Lake Weelhamby, Southwest Australia. D. G. Murray, analyst (Simpson, 1931–32).
(3) Leucophosphite, synthetic. Haseman, Lehr, and Smith (1950).
(4) Theoretical composition of synthetic compound of formula $KFe_2'''(PO_4)_2(OH) \cdot 2H_2O$.
(5) Leucophosphite, Sapucaia pegmatite, Brazil; M. L. Lindberg, analyst. A spectrogram (IWS-561) by Harry Bastron shows in addition .X% Mg, .X% Si, .0X% Ba, and a line detected for Cu, Sn and Be.
(6) Analysis 5, recalculated to 100% without insoluble matter.
* Assuming 44 oxygen atoms per cell (4 formulas).

PARAGENESIS

Leucophosphite formed late in the mineral sequence at the Sapucaia granite pegmatite. Minerals formed earlier include quartz, albite, perthite, muscovite, and triphylite. Hydrothermal fluids generated within the pegmatite produced a large variety of secondary minerals. Leucophosphite together with avelinoite occur in well-formed crystals in vugs in frondelite. The close association of the two separate mineral species, one sodium-rich and the other potassium-rich, suggests that, although a limited amount of subsitution in each mineral occurs, the two mineral species do not form a complete mineral series from sodium to potassium end-members, but instead the small amount of leucophosphite present represents potassium in excess over that which will enter into the avelinoite molecule.

Leucophosphite has been synthesized in the laboratory (Haseman, Lehr, and Smith, 1950) at temperatures ranging from 75° to 145° C., at a pH of 2.5 to 6.0, and at phosphate concentrations of 1.0 to 3.5*M*. These data on synthesis are consistent with the low-temperature hydrothermal genesis indicated by the late position of leucophosphite in the observed mineral sequence.

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SECONDARY URANIUM MINERALS AT THE W. WILSON MINE IN THE BOULDER BATHOLITH, MONTANA*

D. O. Emerson and H. D. Wright

Abstract

Secondary uranium minerals found in the W. Wilson mine, near Clancy, Montana, include meta-autunite, meta-uranocircite, meta-torbernite, meta-zeunerite, uranophane, beta-uranophane, phosphuranylite, gummite, and an unidentified mineral, possibly a complex uranium silicate. Uraninite in this "siliceous reef" deposit has been leached and altered by ground water to form the secondary minerals. The deposition of autunite and torbernite as the meta-I hydrate, apparently at normal ground water temperatures, would appear to lower the range of temperature stability previously reported for these minerals. Isomorphous substitution among the four minerals of the meta-torbernite group may be responsible for this difference in stability. Although isostructural with uranophane, the W. Wilson material of this composition has minor discrepancies in its optical character which may be due to the extra Cu, Ba, or Pb in the mineral.

Introduction

The W. Wilson mine, near Clancy, Montana, provided an excellent opportunity to study the secondary uranium mineralization in a uraninite-bearing sulfide vein deposit close to the surface. Field investigations were begun during the summer of 1952 as part of a program of mineralogical studies of vein uranium deposits in the Boulder batholith, undertaken at The Pennsylvania State University on behalf of the U. S. Atomic Energy Commission. This paper summarizes the chemical, crystallographic, optic, and *x*-ray data on the secondary uranium minerals identified. Their distribution and zoning relative to the primary uranium minerals, the land surface, and the ground water table are discussed in a separate paper. (Wright and Emerson, 1957)

The W. Wilson mine, the largest of several small uranium producers in the northern part of the Boulder batholith, lies about 15 miles south of Helena, Montana. It is a "siliceous reef" type vein deposit in quartz monzonite. The gangue of vari-colored microcrystalline quartz contains small amounts of pyrite, galena, sphalerite, argentite, chalcopyrite, covellite, and uraninite, chiefly as microscopic inclusions.

Uraninite is the only uranium mineral recognized as primary. Although all of the uranium is thought to have been deposited originally as uraninite, nearly all of it is now in the form of secondary minerals. These are found both in scattered patches in the vein proper, and disseminated in the wall rock.

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RECENT WORK

The geology of the area west of Clancy was mapped by Roberts and Gude (1951) of the U. S. Geological Survey. They reported the occurrence of pitchblende, rutherfordine, uranophane, volgite, torbernite-zeunerite, autunite-uranocircite and gummite in the outcrop of the reef now being developed by the W. Wilson mine. A more recent study, made after considerable underground development, was conducted by Meschter (1953) of the U. S. Geological Survey. He found pitchblende, meta-torbernite, meta-zeunerite, autunite, uranophane, gummite, uranocircite, and phosphuranylite.

Thurlow and Reyner (1951) of the U. S. Atomic Energy Commission noted the presence of pitchblende, autunite, torbernite, gummite and possibly zeunerite, phosphuranylite and uranophane in the open cuts along the reef.

SPECTROSCOPIC ANALYSIS

Quantitative analysis of compounds rich in uranium by the spectrographic method is difficult due to the masking effect of the numerous lines of the complex uranium atom. The carrier-distillation method, as described by Scribner and Mullin (1946), was used to suppress the uranium spectrum. This method makes use of the order of volatilization of elements in the arc. Zirconium, hafnium, and most of the rare earths are the only elements reported to be less volatile than uranium. A carrier —in this case Ga_2O_3—mixed with the sample "sweeps out" the more volatile elements and the majority of the uranium remains in the electrode.

Since information could not be found in the literature on the application of the carrier-distillation method to the analysis of uranium phosphates, arsenates and silicates, some experimentation was carried out by Dr. H. L. Lovell and Mr. H. Grendon in the spectroscopic laboratories of the University to develop a suitable procedure for these minerals. A standard exposure (120 seconds at a 13 amp. spark current, using five milligrams of a uranium mineral sample mixed with five milligrams of graphite) was found to produce, as expected, an extremely heavy response of uranium lines and was not usable for semi-quantitative studies.

Exposure tests were made on the 1:1 mixture of Ga_2O_3 and sample. The uranium interference in exposures of 60 seconds and longer was too great for semi-quantitative analysis. When 30-second exposures were made the uranium lines were present but were confined to the 5th to 7th sector steps. The other elements in the sample showed clearly above this low uranium background. This 30-second exposure time was chosen, and five samples and a standard mineral were exposed. The senior author read these first plates and found the concentration estimates of some of the elements too low when compared with the usual graphite standards.

A set of synthetic uranium standards with known amounts of 25 elements was prepared, mixed in 1:1 ratio with Ga_2O_3, and exposed for 30 seconds. The density values obtained from these plates were used to estimate the element concentration in the uranium minerals. The ratio of Ga_2O_3 to sample was varied from 1:1 to 1:5 and uranium interference was found least objectionable at the 1:1 ratio.

Both major and trace elements were sought in each sample. The standardization samples contained Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, N, P, Pb, Sb, Si, Sn, Ti, U, V, and Zn. The amounts of these and 12 others, Au, B, Ca, Ge, K, Li, Na, Rb, Th, W, Y and Zr, were semi-quantitatively determined. In the study of the synthetic oxide mixtures in uranium matrix, serious variations from the expected intensities appeared in Ca, P, and Cu, when their concentration was greater than 0.1 per cent. This suggests that elements present in the larger concentrations tend to be held back with the uranium. It is not clear whether the effect is due to the nature of these particular elements or to their concentration, but the study of synthetic mixtures indicates that concentration is the major factor. Ti was found to be distinctly retarded and As, H, Ni and Sb showed a reduced sensitivity.

It appears that for trace element studies the method described above produces fairly reliable information. For major elements the percentages reported tend to be low and ratios of the major elements cannot be closely relied upon. Further standardization of this spectroscopic technique is needed and the standards should be prepared in a matrix more nearly like the uranium minerals.

SECONDARY URANIUM MINERALS

The brightly colored yellow, green, and orange secondary uranium minerals occur in pseudomorphous replacements of uraninite deposits along fractures and cleavages of the wall rock minerals, and well formed crystals growing in open fractures in veins and wall rock. The mineralogy is complex due to the compositional and structural variability and the abundance of fine-grained intergrown mixtures. Hydrous oxides, arsenates, phosphates, and silicates of uranium are present. Most of the minerals have variable water content and two or three structural changes which accompany dehydration.

The chemical formulas used for the minerals are taken from the *Glossary of Uranium- and Thorium-Bearing Minerals* (Frondel and Fleischer, 1955). The 6th and 7th editions of *Dana's System of Mineralogy*

(Palache, et al, 1951) and the *Tables of Uranium and Vanadium Minerals Which are Largely of Secondary Origin* (Gruner and Gardiner, 1952) provided optical and crystallographic data. Much of the systematic study of the uranium minerals has taken place during the past 10 years. New data are accumulating constantly, and continual revisions are necessary. Many of the earlier names and descriptions have been discarded, and several new species have been described. Descriptions in older publications are often incomplete or contain inaccuracies. The authors were fortunate to be able to compare their mineral descriptions with those tabulated by Dr. Clifford Frondel, which are in preparation for publication and represent the latest and most comprehensive compilation of this information available.

The minerals identified in samples from the W. Wilson mine are meta-autunite, meta-uranocircite, meta-torbernite, meta-zeunerite, phosphuranylite, uranophane, and beta-uranophane. The species contained in the fine-grained "gummite" (please refer to the terminology of "gummite" below), other than varying amounts of the last three minerals named above, have not been positively identified but are probably of the hydrous oxide group.

Rutherfordine and volgite, reported by Roberts and Gude (1951), were not found.

META-TORBERNITE GROUP

Four members of the meta-torbernite isostructural group are common in the W. Wilson deposit. These fit the general formula $A(UO_2)_2\,(XO_4)_2 \cdot nH_2O$ and are the Cu, Ca, and Ba phosphates, meta-torbernite, meta-autunite and meta-uranocircite, and the Cu arsenate, meta-zeunerite. A good summary of the structure and the various transitions due to hydration is given by Palache, et al (1951). One problem in the study of these minerals is that the transitions from one form to another occur near room temperature. The transition from the meta-I structure to the fully hydrated form is reversible in the case of autunite but may not be so in torbernite, zeunerite, and uranocircite. With the large number of samples collected, it was impractical to take the precautions in sampling and shipping necessary to preserve the natural hydration state of the minerals, and in all cases the meta-I structure was the only one found during the laboratory study. However, distortions and cracks due to dehydration were not observed and all of the species may occur in the mine in the meta-I state of hydration. The ease of base exchange in this type of structure was shown by Fairchild (1929) who replaced the Ca of autunite with Na, K, Ba, Mn, Ca, Ni, Pb and Mg by soaking the autunite flakes in solutions containing these elements.

Because of the difficulty of determining the refractive index of the vibration direction perpendicular to the cleavage in these platy minerals, the values listed for the extraordinary ray and the birefringence were obtained from only one sample.

Meta-autunite I	$Ca(UO_2)_2(PO_4)_2 \cdot 2\frac{1}{2}$ to $6\frac{1}{2}$ H_2O
Color:	Yellow to greenish yellow.
System:	Tetragonal.
Habit:	Thin tabular (001), usually square in outline. Subparallel growth gives rise to micaceous aggregates. See Fig. 1.
Oriented growth:	Parallel growth with meta-torbernite is common.
Forms:	(001) and (110) common, (010), (120)?
Cleavage:	(001) perfect, (110) good, (010) and (100) traces seen.
Inclusions:	Irregular red-brown masses of high positive relief are common. Colorless needles of high positive relief are parallel to (010) and (100). Some iron stains.
Fluorescence:	Bright yellow-green
Optics	Anomalously biaxial due to strain.

$n_{\text{Na and white}}$		Orientation	Pleochroism
α 1.594	± 0.002*	*c*	colorless
β 1.604–1.608	± 0.002		light yellow
γ 1.605–1.610	± 0.002		light yellow

Birefringence: $\gamma - \alpha = 0.011$.

Biaxial negative: $2V = 0$–$5°$.

X-ray:

Yellow meta-autunite $n_\gamma = 1.606$.

$d_{(\text{meas})}$ Å	8.33	3.60	3.48	3.22
I	10	9	9	8

Green meta-autunite n_γ 1.606

$d_{(\text{meas})}$ Å	8.42	3.63	3.58	3.20
I	10	10	10	9

Analysis: Semi-quantitative spectroscopic analysis

Yellow meta-autunite

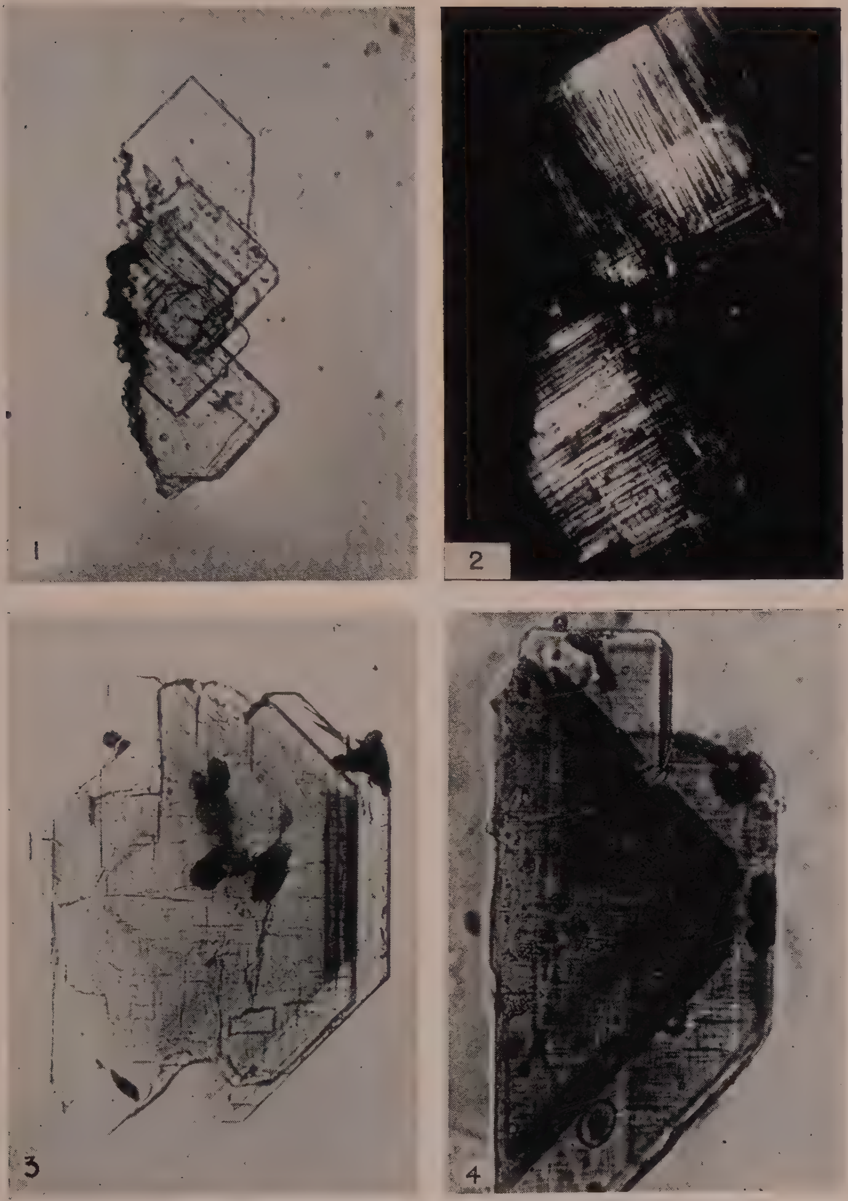
>10%	U, P
1–10%	Ca
0.1–1%	Si, K
0.01–0.1%	Al, Ba, Co, Cu, Fe, Ge, Li, Pb, Na, Sr
0.001–0.01%	Ag, B, Mg

Green meta-autunite

>10%	U, P
1–10%	Ca
0.1–1%	Ba, Cu, K, Si
0.01–0.1%	Al, Co, Fe, Li, Na, Pb
0.001–0.01%	Ag, B, Ge, Mg, Mo

* ±0.002 indicates the precision of a single measurement.

X-ray and spectroscopic data on minerals from the W. Wilson mine indicate that isomorphous substitution may occur among the members of the meta-torbernite group.



Photomicrographs of Meta-torbernite Group Minerals
The (001) plane is parallel to the photograph

Fig. 1. Aggregate of yellow meta-autunite crystals. The group is 0.7 mm. long. Magnified about 80×.

Fig. 2. Aggregate of greenish-yellow meta-uranocircite crystals in crossed polarized light showing the "gridiron" twinning. The group is 1.6 mm. long. Magnified about 50×.

Fig. 3. Aggregate of green meta-torbernite crystals. The group is 0.78 mm. long. Magnified about 80×.

Fig. 4. A crystal of green meta-zeunerite showing phantom outlines. The crystal is 0.81 mm. long. Magnified about 100×.

Most of the meta-autunite has n_γ near 1.605 in the basal section, but some grains approached 1.610. This variation is well within the range recorded in the literature (Palache, et al, 1951). It is not possible to distinguish meta-autunite from meta-uranocircite visually or optically except by the use of index oils. The green color of some of the meta-autunite is probably due to the isomorphous subsitution of Cu or Ba, as suggested by the analysis.

Meta-uranocircite $Ba(UO_2)_2(PO_4)_2 \cdot 8H_2O$.
Color: Yellow-green to yellow.
System: Tetragonal.
Habit: Thin flakes parallel to the fracture surface and in radiating clumps, in the middle of which the flakes are perpendicular to the surface of deposition. Also as individual flakes around grains in the wall rock.
Forms: (001), (110), (010)
Cleavage: (001) perfect, (100) and (010) distinct
Fluorescence: Strong yellow-green
Optics: Anomalously biaxial due to strain

	$n_{\text{Na and white}}$		Orientation	Pleochroism
ϵ or X	1.610	±0.002	*c*	colorless
ω or Y	1.612–1.624	±0.002		pale yellow
ω or Z	1.612–1.624	±0.002		pale yellow

Birefringence: $\omega - \epsilon = 0.012$
Biaxial negative: $2V = 0-5°$
Shows sets of twin lamelle parallel to (100) and (010); these resemble the "gridiron" twinning of microcline (Fig. 2). Nuffield and Milne (1953) suggest that this is due to variation in the zeolite-type hydration of the mineral and is not a structural twinning

X-ray:

$d_{(\text{meas})}$Å	8.52	3.61	3.22
I	10	10	9

Analysis: Semi-quantitative spectroscopic analysis

>10%	U, P
1–10%	Ca, Ba
0.1–1%	Si, Fe, Al, As, Pb, Cu
0.01–0.1%	Mn, Cr, Mo, Ni
0.001–0.01%	Mg, Ag, Be

Samples which were greenish-yellow and showed the twinning had an ordinary index as low as 1.612. For the purpose of this study, all flakes which fit the properties of the meta-autunite to meta-uranocircite series and had an index below 1.612 were classified as meta-autunite regardless of color. The sample submitted for analysis was homogeneous to *x*-rays and the Ca, present in significant amount, may be present in Ba positions.

Meta-torbernite $Cu(UO_2)_2(PO_4)_2 \cdot 4-8H_sO$
Color: Green
System: Tetragonal

Habit: Well formed crystals, thin to thick tabular (001), usually square in outline; rarely pyramidal. Subparallel growth in micaceous aggregates is common. See Fig. 3.

Forms: (001), (010)?, (111)?, (101)?

Cleavage: (001) perfect, (100) distinct.

Inclusions: Irregular colorless inclusions of $n=1.616$ are common. Also iron stains.

Fluorescence: None.

Optics:

n_{Na}	Orientation	Pleochroism
ω 1.626 ± 0.002		green
ϵ about 1.625	c	blue

Birefringence: $\epsilon - \omega$ about 0.001. In white light the indices are slightly higher and there is an abnormal purple interference color. Uniaxial positive or negative.

X-ray: Sample No. 2764, 120 foot level.

$d_{(meas)}$Å	8.26	8.93	3.63	3.45	3.21
I	10	9	10	9	9

Sample No. 425.

$d_{(meas)}$Å	8.76	3.66	3.23
I	10	10	9

Analysis: Semi-quantitative spectroscopic analysis.

Sample No. 2764, 120 foot level.

>10%	U, P
1–10%	Cu
0.1–1%	Al, Ca, Si
0.01–0.1%	Ba, Co, Fe, Mg, Pb
0.001–0.01%	Ag, Mn

Sample No. 425, 70 foot sub-level.

In *Dana's System of Mineralogy*, (Palache *et al.*, 1951), the pleochroism of meta-torbernite (ω=sky blue, ϵ=green) is reversed. This error has persisted from the earlier literature and should be corrected.

Interlayered parallel growth of meta-torbernite and meta-autunite is often seen. Thus the calcium found in meta-torbernite by spectroscopic analysis may be due to intermixed meta-autunite rather than isomorphous substitution. Meta-torbernite overgrowths on meta-uranocircite were noted in several samples.

Isomorphism between meta-zeunerite and meta-torbernite is suggested by Frondel (1955). Spectroscopic analysis of one sample (no. 425) of meta-torbernite, which appears homogeneous from optics and x-ray, shows the presence of considerable As which appears to have substituted for P. The mineral with the relatively high As content is optically negative and has $n_\omega = 1.624$.

Experiments carried out by Hallimond (1920) showed that meta-torbernite formed from aqueous solutions only above 75° C. Although the crystals from the W. Wilson deposit may have become dehydrated on removal, this seems unlikely due to the lack of cracks and turbidity which normally are found when natural torbernite is dehydrated to the meta-I structure. It also seems unlikely that these crystals were deposited from solutions as warm as Hallimond suggests because all evidence strongly indicates movement and deposition by shallow-circulating ground water. It is possible that impurities in the crystals studied forced the meta-I structure to form, and more recent experimental work may already have lowered the formation temperature reported by Hallimond.

Meta-zeunerite $Cu(UO_2)_2(AsO_4)_2\cdot 8H_2O$.
Color: Green.
System: Tetragonal.
Habit: Tabular to scaly (001). Some rectangular outlines. Shows phantom outlines (Fig. 4) and occasionally appears as a parallel (001) overgrowth on meta-uranocircite.
Forms: (001), (010), (110).
Cleavage: (001) perfect, (100) distinct.
Fluorescence: None to weak yellow-green.

	n_{Na}	n_{white}	Pleochroism
ω	1.634 ±0.002	1.634	green.
ϵ	1.624–1.628±0.002	1.624	colorless.

Birefringence: $\omega-\epsilon=0.008$.
Uniaxial negative.

X-ray:

$d_{(meas)}$ Å	8.36	8.86	3.64	3.45	3.20
I	10	9	10	9	9

Analysis: Semi-quantitative spectroscopic analysis.

>10%	U, P
1–10%	Ca, As, Ba, Cu
0.1–1%	Si, Fe, Al, Pb
0.01–0.1%	Cr, Mo, Ni
0.001–0.01%	Mg, Mn, Ag, Be

According to Frondel (1951), meta-zeunerite is the expected form of the material. Meta-zeunerite and meta-uranocircite were noted to have developed, intermixed, on the iron-stained fracture surfaces of several samples.

Fine-Grained Secondary Minerals

Well crystallized samples of the fine-grained yellow minerals are rare, and the largest crystals seldom exceed 0.5 mm. in length. Some of these minerals, uranophane, beta-uranophane and phosphuranylite commonly occur as fine-grained aggregates and form a significant part of the "gummite" (see discussion of "gummite" below).

Uranophane $Ca(UO_2)_2(SiO_3)_2(OH)_2\cdot 5H_2O$.
Color: Yellow.
System: Orthorhombic.

Habit: Well formed, very small radiating laths. Average crystal size 0.1 mm.×0.005 mm.×0.004 mm. Also shown by *x*-ray identification to form as a yellow powder, amorphous under the microscope. See Fig. 5.

Forms: (100), (010), (011)?

Cleavage: (100) and (010), one perfect, the other fair.

Inclusions: Irregular opaque inclusions occur rarely.

Fluorescence: None.

Optics:

$n_{\text{Na and white}}$	Orientation	Pleochroism
α 1.627±0.002		colorless.
β 1.649±0.002	*c*	yellow.
γ 1.660±0.002		yellow-green.

Birefringence: $\gamma-\alpha=0.033$.

Biaxial negative: 2V=60°.

Dispersion: $r>v$ moderate. Abnormal blue interference color due to dispersion.

X-ray:

$d_{(\text{meas})}$Å	7.89	3.95	2.98	2.90
I	10	10	9	9

(For greater detail see Table 1).

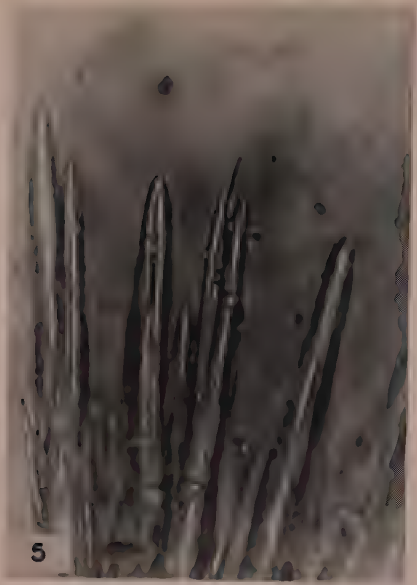
Analysis: Semi-quantitative spectroscopic analysis.

>10%	Si, U
1–10%	Ca, Ba, P, Cu
0.1–1%	Fe, Al, Pb
0.01–0.1%	Mn, Cr, Mo
0.001–0.01%	Mg, Ag, Be

Published information on uranophane, such as Larsen *et al.* (1926), includes optical data which as shown below are incompatible with the optical character of the W. Wilson uranophane.

	Uranophane from Lusk, Wyo. (Larsen et al, 1926)	W. Wilson uranophane
α	1.642	1.627
β	1.665	1.649
γ	1.672	1.660
	$r<v$	$r>v$
2V	37–45°	60°
Orientation	Elongated parallel to Z.	Elongated parallel to Y.

The reason for the optical discrepancy is not known. It may conceivably be related to the extra Cu, Ba or Pb indicated by the analysis of W. Wilson uranophane. The *x*-ray powder photograph of the W. Wilson mineral is identical to the pattern from the spindle of the U. S. Geological Survey's uranophane sample #1313, and Dr. Frondel (personal communication) reported that the W. Wilson uranophane is identical structurally with uranophane in the Harvard University collection.



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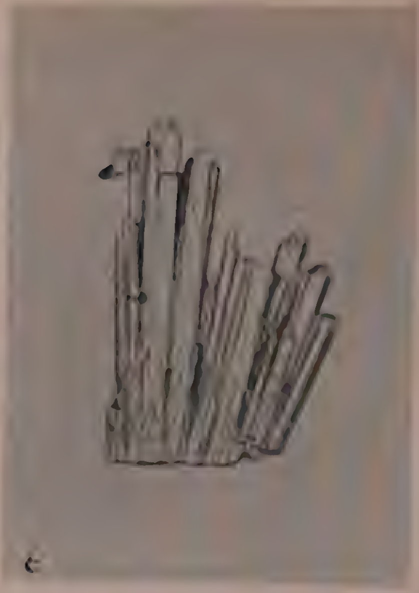

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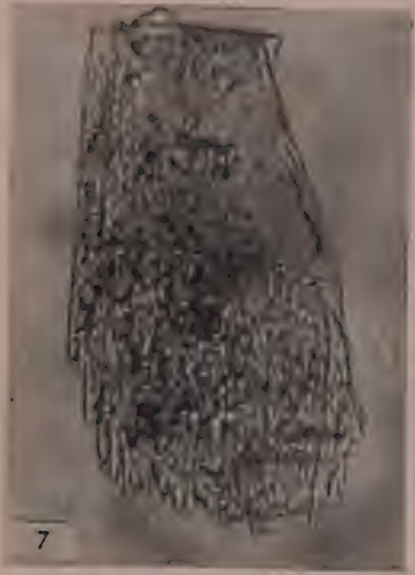

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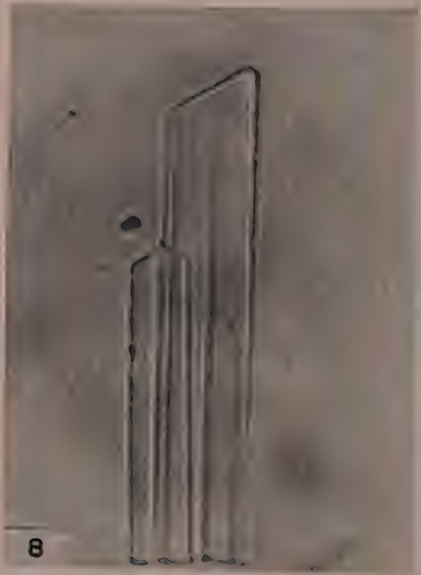

8

Photomicrographs of Secondary Uranium Minerals

FIG. 5. A cluster of uranophane needles showing their terminations. The (001) plane is parallel to the photograph. The field of the photograph is 0.1 mm. long. Magnified about 750×.

FIG. 6. A cluster of beta-uranophane laths. The (010) plane is parallel to the photograph. The field of the photograph is 0.5 mm. long. Magnified about 150×.

FIG. 7. A local fragment of phosphuranylite showing crude crystal outlines and cleavage traces. The (001) plane is parallel to the photograph. The field of the photograph is 0.2 mm. long. Magnified about 375×.

FIG. 8. Parallel crystals of mineral "X". This orientation gives a centered Bx$_a$ figure. The field of the photograph is 0.2 mm. long. Magnified about 375×.

Beta-uranophane $Ca(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$.

Color: Yellow.

System: Monoclinic, β=about 94°.

Habit: Well formed crystals, moderately thick, tabular parallel to (010). Aggregate growth parallel to (010) is common. Average single crystal size 0.1 mm.×0.04 mm.×0.02 mm. Commonly in radial aggregates. See Fig. 6.

Twinning: Occasional twinning on the c axis.

Zoning: Crystal zoning is seen in (010) section with zone boundaries parallel to (100) and (001).

Forms: (100) (001) (100) very small.
(010) (011) (101)

Cleavage: (010) perfect, (100) poor.

Inclusions: Rare, some iron stains.

Fluorescence: None.

Optics

	n_{Na}	n_{white}*	Pleochroism
α	(1.652–1.656) ±0.002	1.652	colorless.
β	(1.678–1.682) ±0.002	1.680	light yellow.
ω	(1.682–1.686) ±0.002	1.683	light yellow.

Orientation: b=X, $c \wedge Y_{Na}=30°-40°$.

Birefringence: $\gamma-\alpha$ about 0.030.

Biaxial negative: $2V=10-20°$

Absorption: Z=Y>X.

Dispersion: $r>v$ very strong, crossed, abnormal interference colors.

X-ray:

$d_{(meas)}$Å	7.78	3.84	3.47	3.16
I	10	9	8	8

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* These are approximate values because of strong dispersion.

The zoning, similar to that reported by Steinocher and Novacek (1939) for beta-uranotile (=beta-uranophane), is attributed to compositional variations and is probably not due to a change in the hydration state.

A ten milligram sample for spectrographic analysis could not be obtained.

Phosphuranylite $Ca(UO_2)_4(PO_4)_2(OH)_4 \cdot 7H_2O$.

Color: Dark yellow.

System: Orthorhombic (Hogarth and Nuffield, 1954).

Habit: Microscopic rectangular basal plates. Crystal outlines are not well formed. See Fig. 7.

Fluorescence: None.

Optics:

	n_{Na}	n_{white}	Pleochroism
α	1.672 ±0.002	1.668	colorless.
β	1.688–1.696 ±0.002	1.684–1.692	dark yellow.
γ	1.688–1.696 ±0.002	1.684–1.692	dark yellow.

Birefringence: $\gamma-\alpha=0.016-0.024$.

Biaxial negative: $2V=10–35°$ $r>v$ strong.

X-ray:

$d_{(meas)}$Å	7.83	3.95	5.80	2.87
I	10	9	8	8

TABLE 1. *X*-RAY DIFFRACTION POWDER PATTERN OF URANOPHANE CORRECTED FOR FILM SHRINKAGE. CuKα RADIATION

d(meas.) Å	*I*	*d*(meas.) Å	*I*	*d*(meas.) Å	*I*
7.89	10	2.185	5	1.446	2
6.58	7	2.096	5	1.3849	1
5.40	7	2.036	2	1.3662	1
4.78	8	1.967	5	1.3467	1
4.26	3	1.908	4	1.3221	1
3.948	10	1.864	4	1.2630	1
3.579	5	1.821	2	1.2423	2
3.489	5	1.771	4	1.1859	1b
3.414	2	1.742	4	1.1487	1b
3.200	8	1.716	1	1.0811	1
3.075	2	1.688	1	1.0702	1
2.981	9	1.654	2	1.0515	1
2.898	9	1.606	1	1.0242	1
2.682	7	1.583	1	0.9536	1
2.625	7	1.563	1	0.9110	1
2.564	2	1.533	2	0.8914	1
2.511	3	1.488	2	0.8663	1
2.411	2	1.464	1	0.8544	1

Contrary to the data of Frondel (1950) and Palache *et al.* (1951), who report Z perpendicular to the tablets, X is perpendicular to the plates in the W. Wilson material. The orientation found by the authors agrees with the two determinations made by Larsen (1921), and considering the pleochroism, optic sign, and pseudo-tetragonal nature of the mineral, the orientation with X perpendicular to the plates appears more consistent to the authors.

A ten milligram sample for spectroscopic analysis could not be obtained.

Mineral "X"

Color:	Yellow.
System:	Orthorhombic?
Habit:	Well formed, very small radiating laths. Crystal size about 0.3 mm.×0.02 mm×0.01 mm. Parallel growths are common. See Fig. 8.
Forms:	If the length = *c*, width = *b*, and thickness = *a* then (100) (010) (011)? are present.
Cleavage:	(100) and (010) perfect.
Inclusions:	Rare.
Fluorescence:	None.

Optics:	n_{Na}	Orientation	Pleochroism
	α 1.71±0.01		colorless.
	β 1.87±0.01		colorless.
	γ 1.92±0.01	*c*	light yellow.

Birefringence: $\gamma-\alpha=0.21$.
Biaxial negative: 2V=55°
Dispersion: $r>v$ moderate.

X-ray:	$d_{(meas)}$Å	7.67	3.37	3.83
	I	10	8	7

(For additional *x*-ray data see Table 2.)

Analysis: Semi-quantitative spectroscopic analysis.

>10%	U
1–10%	Si, Ca, Cu, Mo
0.1–1%	Fe, Al, Pb, Ba
0.01–0.1%	Cr
0.001–0.01%	Mg, Ag

Only one specimen of this mineral was found in the W. Wilson mine. The sample was collected by Mr. Buford Miles while he was working in the mine near the 50 foot sub-level. Radiating clusters of the lath-like crystals occur in open fractures with a few crystals of meta-torbernite.

The mineral lost about 5% of its weight when heated at 75° C., and no further loss occurred at 110° C. The *x*-ray powder photograph did not match anything, known or unidentified, in the file of uranium minerals at Harvard University (C. Frondel, personal communication). Mineral "*X*" is apparently a new species and the spectroscopic analysis indicates that it is possibly a complex uranium silicate. More accurate chemical data are needed to determine the composition of this mineral and establish it as a new species.

The authors have identified this same mineral in a sample from Marysvale, Utah.

TABLE 2. *X*-RAY DIFFRACTION POWDER PATTERN OF MINERAL "X"

Not corrected for film shrinkage. CuKα radiation

d(meas.)	*I*	*d*(meas.)	*I*	*d*(meas.)	*I*
7.67	10	2.903	5	1.696	1b
6.60	5	2.710	1	1.612	2
4.98	5	2.128	4	1.566	5
4.49	5	2.075	4	1.540	1
3.834	7	2.031	4	1.497	1
3.369	8	1.956	6	1.433	1
3.220	6	1.884	6	1.3139	1
3.139	6	1.800	1b	1.2642	1
2.978	5				

GUMMITE AND "GUMMITE"

Gummite is a loosely defined generic term referring to the alteration products about uraninite. It represents the final stages of oxidation and hydration, and its mineral composition has been shown by Frondel (1956) to vary widely. Frondel (1956, p. 542) found that it was possible, using *x*-ray, optical, and thermal methods, to identify the components of nearly all of about 100 specimens of gummite examined with already known uranium minerals, and that "gummite and its analogues virtually disappear as units of description" if these methods are applied. Geologists in the Boulder batholith have used the term as a convenient field name to describe all amorphous or very fine-grained yellow secondary minerals, whether or not they appear to have replaced uraninite directly. Closely associated with some of the uraninite fragments is a glassy orange to yellow material which fits the more common usage of gummite. The field term "gummite," used in quotation marks, has been retained by the present authors in the study of the distribution of the uranium secondaries (Wright and Emerson, 1957), to refer to the fine-grained yellow material lacking a vitreous luster and commonly occurring at some distance from original uraninite sites.

The orange-yellow vitreous gummite occurs very sparingly in the W. Wilson deposit and little material could be collected. This material gave a poor *x*-ray pattern with faint lines at 3.21 and 3.34 Å and very weak, broad lines at 4.02, 4.12 and 7.83 Å. When the material was heated at 500° to 600° C. for several hours in an attempt to crystallize it and sharpen the *x*-ray lines it turned a deep red but did not melt. No clear powder pattern could be obtained and only one weak line with a spacing of 3.32 Å remained. This gummite is anisotropic with indices of refraction around 1.70. A spectroscopic analysis shows a significant amount of Si, Sb, and As.

Much of the fine-grained yellow "gummite" is a mixture of uranophane, beta-uranophane and phosphuranylite. However, a number of lines which cannot be attributed to these minerals appear in the *x*-ray patterns. The wide variation in the peak positions and heights of the *x*-ray diffractometer patterns indicate a great variability in the composition of the "gummite." Spacings which could be due to clarkeite ($UO_3 \cdot nH_2O$?), fourmarierite ($PbO \cdot 4UO_3 \cdot nH_2O$) and epiianthinite ($UO_3 \cdot 2H_2O$) were found in some of the patterns. The high refractive indices of some components in the "gummite" are in the proper range for these minerals (1.8–2.0), but positive identifications could not be made. Two samples were spectroscopically analyzed and these yielded the following results:

	#1	#2
>10%	U	U
1–10%	Ca, P, Si, W	Ca, P, Si
0.1–1%	Ba, Pb, Sb, K	K, Pb, W
0.01–0.1%	Al, Co, Cu, Fe, Mn, Mo, Na, Rb	Al, Ba, Co, Cu, Fe, Mo, Na, Rb, Sb
0.001–0.01%	Ag, Mg	Ag, Mg, Mn

The analyses show the variability in the gummite and indicate that it is composed primarily of hydrous uranium oxides, silicates, and phosphates. The surprising abundance of tungsten cannot be explained by the authors.

A brief study of the fine-grained yellow "gummite" material was made with the electron microscope. Both powder and surface replica techniques were used for the fine-grained secondaries and in both cases the majority of the material showed no distinct crystal outlines. An occasional grain showed parallel edges, probably due to cleavage, and a few 90 degree crystal or cleavage corners could be seen. The surface replicas showed cleavage in poorly developed crystal laths. The larger grains are about two to six microns across.

Surface replicas of the gummite were difficult to obtain because of the small size of the samples. The largest continuous fracture surface of this glassy material measured two millimeters across. On this surface the electron microscope showed areas of irregular fractures and a few pockets of lath-like needles which are about 0.5 to 1.0 microns long and 0.1 micron thick.

CONCLUSIONS

Four members of the meta-torbernite structural group, meta-autunite, meta-uranocircite, meta-torbernite and meta-zeunerite, occur in the W. Wilson deposit. Uranophane, beta-uranophane, phosphuranylite, gummite and an unidentified mineral occurring in yellow needles of high refractive index are also found. All of the minerals for which chemical data could be obtained show variations from the ideal formulas, due probably to one or more of three factors: contamination, interlayering, and isomorphism. Contamination is the probable source of iron in the uranophane. Interlayering of meta-autunite and meta-torbernite was observed, and may occur in many more cases than were recognized, since it can be observed only under unusual circumstances. Isomorphous substitution is suggested as the main cause of the variation in Ba, Ca, and Cu as well as P and As in the meta-torbernite structure minerals.

This deposit is possibly unique in that no minerals of the hydrated torbernite structure were found and evidence suggests that only the meta-torbernite type minerals were deposited. This may be due to the isomorphous compositional variations in the meta-autunite and meta-torbernite, although there may have been recent unpublished experimental work, unknown to the authors, demonstrating temperatures for the stability field lower than those reported earlier.

The discrepancy between the optical data on the W. Wilson uranophane and the published data on that mineral may be due to the extra Cu, Ba or Pb. The structural identity with normal uranophane is shown by the *x*-ray powder patterns.

Optical study of the meta-torbernite showed the pelochroism to be the reverse of that listed in the seventh edition of *Dana's System of Mineralogy* (Palache, 1951). Also, phosphuranylite is described as having Z perpendicular to the tabular development while the W. Wilson material has X perpendicular to the tablets.

Mineral "*X*", the yellow needles of high refractive index, is probably a complex hydrated uranium silicate on the basis of one spectrographic analysis. Its structure is not similar to any of the known uranium minerals. More accurate chemical data needed to establish this mineral as a new species will be difficult to obtain with the very limited amount of material available.

The "gummite" of the W. Wilson deposit is a mixture of various amounts of uranophane, beta-uranophane and phosphuranylite with several unidentified minerals. The material is composed of significant amounts of Ba, Ca, K, P, Pb, Si, W, and U.

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Reference mineral specimens were provided by Dr. George Switzer of the U. S. National Museum, and standard *x*-ray spindles were loaned by the U. S. Geological Survey's Trace Elements Laboratory. Dr. Clifford Frondel kindly authorized the reading of pertinent parts of his manuscript on the secondary uranium minerals. Appreciation is expressed to Mrs. Edith Emerson, Mrs. Jane Thornton, and Messrs. David Fenstermacher and Herbert Wilson, who aided in the laboratory investigations.

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MEMORIAL OF GEORGE HAROLD ANDERSON

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Dr. George Harold Anderson, who was born in Elko, Nevada, on November 21, 1893, passed away in New York February 16, 1956. He took his A.B. and A.M. degrees at Stanford University in 1917 and 1920, respectively, later studying both at Harvard and at the University of Colorado, and then took his Doctor's degree in geology at the California Institute of Technology in 1933. Upon graduation from Stanford he was elected to Sigma Xi and to Phi Beta Kappa.

Dr. Anderson became intensely interested in the problems of grani-

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tization. His doctor's thesis was devoted to a study of such phenomena in the northern Inyo range of California. This thesis was published, in the *Bulletin of the Geological Society of America*, volume 48, pages 1 to 74, 1937. He also devoted considerable time to other problems in this same general area in California.

However, Dr. Anderson's active mind was turned later to more commercial matters. For three years, he was in charge of exploration for titanium ores in the San Gabriel mountains, north of Los Angeles, for the du Pont Company, and then he joined the staff of the Texas Power and Light Company at Dallas. The management of that company had devoted their energies to developing the natural resources of Texas and especially in the starting of a blast furnace and steel plant to supply steel for the ever-growing oil industry of that great state.

Dr. Anderson was in charge of the development of the east Texas iron ore fields which had been examined and condemned by a generation of earlier geologists. He lived to see the establishment of a great steel industry based on those ore deposits.

During the second world war, he spent a great deal of time and effort in attempting to get the War Production Board to permit this steel development. After the war, the management of the Texas Power and Light Company saw that the great supplies of natural gas in the State were not sufficient to form entirely the basis for the long range future of Texas expansion. Dr. Anderson initiated an investigation that led the Aluminum Company of America to build their smelter at Rockdale, Texas, using lignite as fuel for the power plant.

His achievements for the Texas Power and Light Company led him up to the office of Assistant to the President, in which capacity he commanded the respect and love of his associates. During his later years, he spent a great deal of his time attempting to bring other major industries to Texas, and so the native of Nevada became an enthusiastic Texan.

Dr. Anderson is survived by his wife, Mrs. Genevieve Anderson, and by three children, two of whom are doctors of medicine.

He was a Fellow of the Geological Society of America, a Fellow of the Mineralogical Society of America, and a member of the Society of Economic Geologists, of the American Association of Petroleum Geologists, and of the American Institute of Mining, Metallurgical and Petroleum Engineers.

MEMORIAL OF NORMAN L. BOWEN

J. F. Schairer, *Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.*

Norman L. Bowen died in Washington, D. C., on September 11, 1956, after an illness of about two years. The passing of this great petrologist and past president of the Mineralogical Society of America will be noted with sadness by his many friends in mineralogy and geology. He leaves his widow, Mary Lamont Bowen of Washington, D. C., and a daughter, Catherine (Mrs. Jerrold Orne) of Montgomery, Alabama.

Like most great men in science, Norman L. Bowen has contributed to both fact and theory. As is the usual case with brilliant scientists, he became recognized as a leader early in his career. By the year 1915, at the age of twenty-eight years, his reputation among petrologists was established when he published a paper on *The later stages of the evolution of igneous rocks.* Besides his many papers reporting the results of phase-equilibrium studies on specific systems of rock-forming minerals, his papers *The problem of the anorthosites* (1917), *Crystallization differentiation in igneous magmas* (1919), *Diffusion in silicate melts* (1921), *Genetic features of alnoitic rocks* (1922), *The reaction principle in petrogenesis* (1922), *The behavior of inclusions in magmas* (1922), and *The origin of ultrabasic and related rocks* (1927) were outstanding contributions to the literature of petrology, which preceded the publication of his monumental book *The evolution of igneous rocks* in 1928. This book has had a profound influence on the younger generation of geologists because it emphasized the importance of the point that sound principles of physical chemistry underlie geological processes. This book has been so much in demand that a new reprint edition has just been issued.

One of the great ideas developed by Bowen is the significance of the reaction principle in petrogenesis. Pentti Eskola of Finland has called it the most important contribution to petrology of the present century. Other great fundamental contributions have been a quantitative discussion of the heat relationships and the quantitative possibilities of incorporation to be expected where magmas intrude and react with country rock, the succession of mineral assemblages to be expected at successively higher temperatures in the metamorphism of impure carbonate rocks, the relations in silicates of ferrous iron, the importance of petrogeny's residua system, and the origin of granites. In addition, the important laboratory contributions of Bowen and his colleagues provide not only a physical-chemical basis for geological processes, but are fundamental contributions to the mineralogy of the rock-forming minerals and have been widely useful as the basic science underlying such important ceramic materials as cements, refractories, and glass, and the chemistry of metallurgical slags.

The desirability of experimental studies in the laboratory as an important adjunct to geological field observations has long been urged by Bowen. Experiment is a necessary check on inference from observations on the natural materials and in turn provides a chemical basis for hypotheses on origins, which may be tested in the field and modified to give a nearer approach to the mechanism of rock genesis. Some have doubted the value of laboratory phase-equilibrium studies in geology because under natural conditions equilibrium is not always attained. The only practical method of studying the physical chemistry of geological processes is to determine equilibrium relations first and then to evaluate the factors that lead to failure of equilibrium under natural conditions, together with the magnitude and direction of their effects.

In the year 1906 the Geophysical Laboratory of the Carnegie Institution of Washington was established for the purpose of studying the problems of rocks and minerals through systematic and sustained experimentation in the laboratory. In the year 1910 Norman L. Bowen came to this laboratory as a young student to use the facilities in making a phase-equilibrium study of a silicate system. He was permitted to use these results for a thesis for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology. For forty-five years he pursued his laboratory studies and carried his results to the field to check them with the rocks themselves.

Norman Levi Bowen was born in Kingston, Ontario, Canada, June 21, 1887. He received his Master of Arts degree from Queen's University in 1907, the Bachelor of Science degree from Queen's University in 1909, the Doctor of Philosophy degree from Massachusetts Institute of Technology in 1912, the Honorary Doctor of Laws degree from Harvard University in 1936, the Honorary Doctor of Science degree from his Alma Mater in 1941, and the Honorary Doctor of Science degree from Yale University in 1951. He was Assistant Petrologist, Geophysical Laboratory of the Carnegie Institution of Washington, 1912 to 1918; Professor of Mineralogy, Queen's University, 1918 to 1920; Petrologist, Geophysical Laboratory, 1920 to 1937; Charles L. Hutchinson distinguished service Professor of Petrology, University of Chicago, 1937 to 1947; Petrologist, Geophysical Laboratory, 1947 until his retirement in 1952. After a year in Clearwater, Florida, following his retirement, he returned to Washington and was still active and had an office at the Geophysical Laboratory until his death.

Bowen's pre-eminence in science is attested by the receipt of many honors both at home and abroad in recognition of his achievements. He was president of the Mineralogical Society of America in 1937 and of the Geological Society of America in 1946. He was elected a member of the American Philosophical Society and the National Academy of Sciences.

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He has been honored abroad by election as a foreign member by the Royal Society (Great Britain), the Finland Academy of Sciences, the Academy Naturwissenshaften (Halle), the Academy Lincei (Rome), the Geological Society of Belgium, and the Indian Academy of Sciences. He has received the Bigsby Medal of the Geological Society of London (1931), the Penrose Medal of the Geological Society of America (1941), the Miller Medal of the Royal Society of Canada (1943), the Roebling Medal of the Mineralogical Society of America (1950), the Wollaston Medal of the Geological Society of London (1950), the Hayden Medal of the Academy of Natural Science of Philadelphia (1953), and the Bakhius Roozeboom Medal of the Royal Netherlands Academy (1954).

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MEMORIAL OF WILLIAM FREDERICK FOSHAG

W. T. Schaller, *U. S. Geological Survey, Washington, D. C.*

Early Monday morning, May 21, 1956, Bill, as William Frederick Foshag was best known to his host of friends and admirers, peacefully passed on, at the age of 62, as a result of too high blood pressure, in the home that he and Mrs. Foshag had planned and built in Westmoreland Hills, Maryland, just outside of the District of Columbia.

He was born on March 17, 1894, at Sag Harbor, Long Island, New York. As a boy, his interest in things geologic was aroused by a neighboring physician's extensive library of books on geology. Later, his parents moved to California where Bill entered the University of California and chose chemistry as his major subject. While an undergraduate, he worked in the laboratory of the Riverside Portland Cement Company, 1917–1918, where his love for minerals was greatly intensified by close contact with the wonderful Crestmore occurrences.

Events moved quickly for him in the next few years: A.B. (Chemistry), 1919; Ph.D., 1923, University of California; assistant curator of mineralogy, U. S. National Museum, 1919; associate editor, American Mineralogist, 1920; and, in 1923, marriage to Merle Crisler who, with their son, William Frederick Foshag, 3rd, survives him. In 1929, Dr. Foshag became Curator of the Division of Mineralogy and Petrology, and in 1948, Head Curator of the Department of Geology, U. S. National Museum. During these years, both the Roebling and Canfield mineral collections, accompanied by substantial financial endowments, were given to the Museum largely as a result of his efforts. The collection of cut and uncut gemstones has also been greatly augmented by his constant endeavors.

In addition to his heavy duties as Curator in the United States National Museum, Dr. Foshag conducted investigations and published many papers on mineralogy, petrology, meteoritics, gemology, volcanology, and collateral subjects. His bibliography numbers more than one hundred published papers and includes descriptions of thirteen new minerals. Though not very robust physically, he always kept up with the best of us in the field. Much of his time was spent studying and collecting at various mineral localities in Mexico, as well as in the United States, until a few years ago when a weakened heart called for severe curtailment of field activities. As part of his Mexican work, he studied and described the cornfield volcano, Parícutin, from its birth in 1943 to its end. His report thereon, written in conjunction with Jenaro González, appeared two months before his death, as U. S. Geological Survey Bulletin 965-D. His analyses of the fumarolic gases and minerals from the volcano

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remain unfinished. Also incomplete is a large report on the minerals of Mexico, as well as a comprehensive report on saline borate minerals. It is hoped that these will be put in shape for publication.

In 1946, four months were spent in Japan supervising the grading, classification, and appraisal for the United States Government of many million dollars worth of diamonds, which had been given by the Japanese people to the Japanese Government to aid its war effort. Shortly thereafter, a study of ancient jade objects found in Central America was made for the Government of Guatemala.

For his meritorious achievements in the mineralogic sciences, Dr. Foshag was awarded the Washington A. Roebling Medal of the Mineralogical Society of America in 1953. In addition to being a charter fellow in our Society, he had also held several offices—associate editor, councilor, vice-president, and president (in 1940). Many of the details of his accomplishments and of his wide interest in earth science are given by Professor Edward H. Kraus in the written record of the Roebling Medal presentation (*American Mineralogist*, vol. 39, 293–295, 1954). Another glowing tribute to Dr. Foshag and his work was placed in the Congressional Record two days after his death by the Honorable H. Alexander Smith, Senator of New Jersey and member of the Board of Regents of the Smithsonian Institution.

On the occasion of the Roebling Medal presentation, Foshag also received a well merited tribute from the Geological Institute of Mexico and from his numerous Mexican colleagues, many of whom he had helped to train, always, as stated in the tribute, "giving his valuable time with unstinting cheerfulness." This last statement, it seems to the writer, carries a thought that is believed to outweigh in actual worth his many accomplishments. Bill had a concept, not held by all curators, that a museum and its contents served best when all facilities were extended to competent applicants. To him, any specimen, no matter how rare or valuable, was most useful when it was fully available for study, and many of us and many institutions have benefited greatly by this wise policy. And always, he was "giving his valuable time with unstinting cheerfulness," whether it was a desired specimen, or an interpretation of a chemical analysis, or a discussion of any phase of mineralogy, or related matters.

Bill and I had much in common—the same teachers in Berkeley (Walter C. Blasdale, Arthur S. Eakle, Andrew C. Lawson), the same love for minerals, for discussions on genetic processes, for talking about California, and many other topics. He had spoken about retiring before his proverbial three score and ten and the Foshags had made tentative retirement plans. His sudden death leaves a great void in our hearts and long will we miss his "unstinting cheerfulness."

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By Marjorie Hooker

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PRESENTATION OF THE ROEBLING MEDAL OF THE MINERALOGICAL SOCIETY OF AMERICA TO ARTHUR F. BUDDINGTON

H. H. HESS *Princeton University, Princeton, New Jersey*

Mr. President, Fellows, Members of the Society and Guests:

I am happy to introduce Arthur F. Buddington to you as Roebling medallist. In awarding this medal the Society honors the recipient, it honors the memory of Colonel Roebling and I believe it does credit to itself in reaffirming its stand that it represents mineralogy in the broadest sense.

This is the 15th time the Society has awarded the medal. It is the third time that both the Roebling medal of the Mineralogical Society and the Penrose medal of the Geological Society have been won by the same man, the other two being Esper S. Larsen, Jr. and Norman L. Bowen. These are certainly men in whose company Buddington would feel comfortable. It was Buddington who introduced Bowen when he was medallist six years ago. This was the occasion when Bowen, in reply to Buddington, referred to himself as the "Canadian goose," in a speech characterized by his usual delightful sense of humor.

I have known Buddington for 30 years, first as a student and then as a colleague. For 20 years we have occupied adjacent offices with open doors between them. From my desk I can see him working at his table. The day rarely passes that we do not debate some current problem. On the lighter side Jene Buddington and I have played hundreds of rubbers of bridge against Annette Hess and Arthur Buddington. I know exactly how Budd overbids his hands and never cease to be surprised when he gets away with it. So I think I can speak with more than usual authority on Budd's achievements.

Buddington is unique in that he has made important contributions in so many such diverse fields. His earliest work was on the Precambrian of Newfoundland. Following service as a sergeant 1st class in World War I, he went to the Geophysical Laboratory. Here he became familiar with experimental and theoretical phase rule chemistry, and produced with Ferguson the akermanite-gehlenite diagram. He has had probably the longest and certainly the most distinguished WAE career on the U. S. Geological Survey extending over 37 years. Well known are his geological and mineral deposits studies on South Eastern Alaska, the Cascade Range in Oregon, the Adirondacks and northern New Jersey.

He is an expert on Rosiwal analysis of rocks, on polished section

ARTHUR F. BUDDINGTON
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study of ore minerals, on structural petrology in the field, on the distinction between metasomatic and magmatic granites, and on the anorthosite problem. He has written excellent papers ranging from such details as the nickel minerals in a deposit in Alaska to broad philosophical concepts such as his presidential address to this society. This dealt with his ideas on the interior of the Earth based on petrological inference and the evidence from seismology.

In the last decade much of his research work has been related to the system Fe_2O_3—FeO—TiO_2 and remanent magnetism of rocks containing minerals in this system. Though perhaps not yet fully recognized he has made a very great contribution by bringing together experience in subsolidus exsolution relations, petrologic concepts on thermal history and magnetic properties of the minerals. There is probably no other living scientist who could cover all three of these fields expertly. As a result an understanding of the phenomena is rapidly being developed which, without Buddington's part in it, might well have been delayed many years.

Finally, perhaps his greatest achievement and the one on which he has worked hardest for the last 36 years, is that of an outstanding and inspiring teacher of petrology.

Mr. President it is an honor to present Arthur F. Buddington as the recipient of the Washington A. Roebling Medal of the Mineralogical Society of America.

ACCEPTANCE OF THE ROEBLING MEDAL OF THE MINERALOGICAL SOCIETY OF AMERICA

ARTHUR F. BUDDINGTON, *Princeton University, Princeton, New Jersey*

Mr. President, Professor Hess, Fellows and Members of The Mineralogical Society of America and Guests:

I was unaware of who was to introduce me until our President announced it. The Society has been very kind indeed to me in having one of my best friends act as my sponsor.

The award of the Roebling Medal by a group of scientists in one's own special field of endeavor makes the recipient have a warm feeling for all his fellows and a deep seated, though humble, appreciation of the very distinguished honor.

I am also grateful for the medal in that it gives me an opportunity to publicly express thanks for the analytical data of the many chemists whose work has been so essential to my studies. I am pleased that this is occurring in Minneapolis, as I am peculiarly indebted to the chemists of the local Rock Analysis Laboratory of the University of Minnesota for their cooperation and accurate work over a period of many years.

My professional lifetime has seen such an extraordinary growth of laboratory and theoretical researches in geochemistry and the development of new instruments for the furthering of the interpretation of the nature and origin of minerals and rocks that the *relative* importance of field studies in which I have taken such pleasure has diminished.

We have but to mention the following to realize the importance of new instrumentation; the universal stage and micropetro fabrics, the mineralographic microscope and mineragraphy, the *x*-ray and crystal structure, *x*-ray diffraction, the differential thermal analysis instrument, and electron microscope in clay mineralogy; the emission spectrograph and spectrophotometer in trace element geochemistry, the mass spectrometer and isotope geology, the geochemistry or geophysics of age determination, chromographic methods in geochemical prospecting, high temperature bombs for silicate or sulphide chemistry with volatiles, and instrumentation suitable for both high temperature and high pressure for experimental metamorphism.

One has difficulty in matching this array with new ideas based primarily on field work. During the past two score years we have had the major development of the theory of secondary enrichment, zoning of metalliferous deposits and of pegmatites, metasomatism and the migration of elements, qualitative geologic thermometry, the systematic sequence of rocks within stratiform sheets and their correlation with mineral sequence, and the systematic variation of regional mineral assemblages with metamorphic intensity of zoning, all based largely on field geology and the use of the petrographic microscope. However, our real understanding of the origin of the diversification and principles of fractional crystallization within stratiform sheets is based on the experimental chemical studies of the silicate systems, and the development of the metamorphic facies concept on theoretical physicochemical principles. With the aid of physical chemistry we are just beginning to get real *quantitative* controls for geologic thermometry, and the necessary physical chemistry for the adequate interpretation of zoning in mineral deposits is still to come.

I believe that the advances in our knowledge and understanding of the sciences of mineralogy, petrology and mineral deposits during the present century has been equal to that of all previous time and that at least half of the material in our present graduate curricula dealing with the mineralogical sciences has been developed during my professional lifetime and is in large part based on geochemistry, geophysics, mathematics and new instrumentation. One may also note that in the current mineralogical literature about half the references are to publications of the immediately preceding 10 years and 80 per cent to the preceding 25 years.

What does this mean for the *geological* mineralogist of the future?

There is no question but that researches in geochemistry will advance the mineralogical sciences at an accelerated rate for many years to come. However, I believe it is also true that every advance in geochemistry requires ever greater knowledge and refinement of our knowledge based on field relationships and the two must go forward together, each reacting on the other. A specimen of rock *can* be treated in the laboratory as an entity in itself. But the significance for geology of the data obtained from it can only be as good as the thoroughness of the knowledge of the nature of the immediate surroundings of the specimen where in place and of its physical and chemical history as read by a field geologist with the appropriate background.

A glance through the recent university catalogues reveals courses in geology departments in the following subjects, the bases for which have been developed during the normal professional life-time of one man; Crystal structure or *x*-ray crystallography; Mineragraphy, Crystal chemistry, Chemistry of silicate systems, Geochemistry of ore solutions, Spectrochemical analysis, Isotope geology, Thermodynamics of rock making minerals, Geochemistry, Quantitative Sedimentology, Universal Stage studies. This suggests that the present day student of the mineralogical sciences may look forward to the development of at least one new field of research in the mineralogical sciences every decade. Since it takes only 10–25 years to develop a new field to the routine working stage where a textbook or university course in the subject is available, the student must be prepared to acquire a working knowledge of several new fields in his lifetime. If interested in creative research he must have the background and maintain a flexibility such that he can be a participant in the development of two or three quite new fields of endeavor. He must furthermore be familiar with the foreign literature for at least three fifths of our major new ideas in the mineralogic sciences have in the past been developed outside of North America.

In looking over the acceptance remarks of former Roebling medalists I found a statement of Professor Paul Niggli which I feel can bear repeating; "the work of the mineralogist and petrologist starts from the study of Nature and is an attempt to apply the teachings of all fundamental sciences to his own very special problems."

What wonderful opportunities the mineralogic sciences afford. One may enjoy oneself in so many ways; there are the deep satisfactions of new insights resulting from laboratory or library studies; the joy of wandering in the high mountains or the pastured lowlands; the pleasure of talk and friendly fellowship with other mineralogists and finally in addition to and beyond all this one may receive the respected and honored Roebling Medal. I thank you.

PRESENTATION OF THE MINERALOGICAL SOCIETY OF AMERICA AWARD TO GEORGE C. KENNEDY*

J. F. Schairer, *Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.*

Mr. President, Fellows and Members of the Mineralogical Society of America, and Guests:

We meet together on this occasion to do honor to one of our younger men in experimental mineralogy. It is a pleasure and privilege to introduce to you at this time our colleague and my personal friend, George C. Kennedy, of the Institute of Geophysics, University of California at Los Angeles.

The laboratories of Harvard University have contributed much to our knowledge of the behavior at elevated pressures of many substances which form a part of the earth's crust. The inspiration of Bridgeman and Birch has led many of the younger men at Harvard into the interesting and important field of research at high pressures.

At the Institute of Geophysics, University of California at Los Angeles, there is a live group of research scientists who have focused their attention on problems of experimental mineralogy and geology. They have been interested in the behavior of earth materials at moderate to very high pressures over a range of moderate to high temperatures, both with and without the presence of water or other volatiles. They have made substantial contributions to our knowledge of earth materials and to the techniques of experimental geology.

Today we have with us one of the younger members of this research group and we meet here to recognize the contributions of George C. Kennedy. He has been chosen for award because of his substantial contributions to our knowledge of the solubilities of materials in steam at high pressures, the role of volatiles and oxides of iron in melts at high temperatures, and the behavior of rock-forming minerals at moderate to very high pressures. He was also chosen because he shows every promise of making many more contributions in the future to enhance our

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* Kennedy, Dr. George Clayton, University of California, Los Angeles 24, Calif. GEOLOGY. Dillon, Mont., Sept. 22, 19. B.A., Harvard, 40, M.A., 41, jr. fellow, Harvard, 42–46, Ph.D. (geol.), 46. Geologist, Alaskan branch, U. S. Geol. Surv., 42–45; physicist, Naval Research Lab., 45; jr. fellow, Harvard, 46–49, asst. prof. GEOL., 49–53, PROF., CALIFORNIA, LOS ANGELES, 53- Fel. Miner. Soc.; fel. Geol. Soc.; Geol. Soc. Wash. Volcanology; contact metamorphism; solubility in gas phase; melting relations in silicate systems; problems in geochemistry, effects of volatiles; stability relations of minerals at high pressures.

George C. Kennedy
Recipient of the Mineralogical Society of America Award.

very imperfect understanding of the behavior of earth materials under extreme conditions.

Mr. President, I take great pleasure in presenting Dr. George C. Kennedy for the Sixth Mineralogical Society of America Award.

ACCEPTANCE SPEECH MSA AWARD

George C. Kennedy, *University of California at Los Angeles, Los Angeles, California*

Mr. President, Dr. Frondel, Ladies and Gentlemen:

It would be less than honest for me not to indicate how pleased I am to receive the award of the Mineralogical Society of America. In part this pleasure stems from the fact that you are also honoring my students and colleagues, whose work and ideas have contributed inmeasurably to every paper I have published.

I would like now to take a leaf from the book of Julian R. Goldsmith, your MSA award recipient of a year ago, who spoke of you as a captive audience. I would like to speak of the difficult and exciting work which lies ahead in the field of experimental Petrology.

Research in several laboratories over the last few years has shown that the mineral phases which exist at the surface of the earth are not the mineral phases to be expected at depths of only a few kilometers or a few tens of kilometers. Indeed, it now appears that the vast majority of all rock forming minerals which appear on the surface of the earth cannot exist at depths of as little as 100 kilometers in the earth's crust, and a very large fraction of the phases undergo transitions at depths of as little as 30 kilometers. It is, however, in these deeper zones of the earth's crust that most magmas form by partial melting and it is probably here that our major differentiation processes take place. The trend of compositions of magmas during crystal differentiation is, of course, very dependent upon the composition of the phases forming and being extracted. It is equally obvious that trends of differentiation in magmas where feldspars are being extracted will be totally different from trends of differentiation in magmas where the dense polymorphs of feldspar such as various of the jade family of minerals are being extracted. I suspect strongly that the solution to vexing problems such as the origin of the alkaline rocks and certain ultramafic complexes, awaits an understanding of the differentiation processes at these depths. The experimental Petrologist then must over the next few years, examine the equilibrium relations between magmas and high pressure phases. This is going to be extremely difficult work but most exciting work, which is certain to yield big dividends. The next decade in Petrology will see advances as marked as has the last.

PRESENTATION OF A CERTIFICATE OF APPRECIATION TO WALTER F. HUNT THE RETIRING EDITOR OF THE *AMERICAN MINERALOGIST*

CLIFFORD FRONDEL, *President of the Mineralogical Society of America*

Today marks the retirement of Professor Walter F. Hunt as Editor of the *American Mineralogist* after 35 years of devoted service. The Mineralogical Society of America was organized on Tuesday, December 30, 1919. The next day the Council of the MSA adopted the *American Mineralogist* as its official journal and appointed Dr. Edgar T. Wherry as its first editor. Dr. Wherry served until December 1921.

Professor Walter F. Hunt, a member of the board of associate editors was then selected as the second editor in 1922.

The *American Mineralogist* started as a magazine for advanced mineral collectors, museum curators, and professional mineralogist. Even in its earliest years the *American Mineralogist* had been coming to serve the professional mineralogists more and more as a medium of publication of their researches, and so it was natural that the Journal should pass over to the Mineralogical Society after the society was formed.

When Professor Hunt became the editor it soon became evident to him that with limited financial resources available, and the oncoming transition of the *American Mineralogist* to the stature of a journal of a scientific society, that the new editor would have to make a considerable sacrifice of his time that he would normally devote to research. The decision to make this sacrifice must have been difficult for the young mineralogist. Well trained in the experimental techniques of mineralogy, petrology and analytical chemistry, and having worked in the Chemical Laboratory of the U. S. Geological Survey, Professor Hunt was keenly interested in studying the physical properties of minerals as a function of their chemical composition and of the rocks in which the minerals were found. That Professor Hunt did decide to assume the responsibility, being well aware of the sacrifice he would have to make, is the reason that I am now speaking to him.

"Professor Hunt, On behalf of the Council of the Mineralogical Society of America and its Fellows and Members, I thank you for your long and distinguished career as the Editor of our Journal. In the 35 years during which you have been the Editor you have raised the quality of the Journal to one of the foremost mineralogical publications of the world. In doing so we recognize the personal sacrifice you made with respect to your own desire to do research, but your efforts have not been in vain. You and we have much to be proud of. We hope that you have derived a keen satisfaction from your labors; the Mineralogical Laboratory and the University of Michigan must share with us in commending you for your noble efforts. It is with a great deal of pleasure that I present you with this certificate of deep appreciation and thanks from the Mineralogical Society of America." It also is my pleasure to inform you that by vote of the Council you have been appointed Editor Emeritus of the *American Mineralogist.*

PROCEEDINGS OF THE THIRTY-SEVENTH ANNUAL MEETING OF THE MINERALOGICAL SOCIETY OF AMERICA AT MINNEAPOLIS, MINNESOTA

C. S. HURLBUT, JR., *Secretary*

The thirty-seventh annual meeting of the Society, held on October 31-November 2, 1956 at the Nicollet Hotel, Minneapolis, Minnesota, was attended by 115 fellows and members. Five scientific sessions were held at which fifty-four papers were presented on Mineralogy, Crystallography, Petrology and Geochemistry.

The annual luncheon of the Society held on November 1 was attended by 185 fellows, members and guests. Following the luncheon, the fifteenth presentation of the Roebling Medal was made to Arthur F. Buddington and the sixth presentation of the Mineralogical Society of America Award was made to George C. Kennedy. The luncheon was also the occasion of the presentation of a certificate to Walter F. Hunt, Retiring Editor of *The American Mineralogist,* in appreciation of his many years of service to the Society.

The Retiring President, Clifford Frondel, addressed the Society on the afternoon of November 1. His subject was *The Mineralogy of Uranium.* At the annual business meeting preceding the presidential address reports were given by the Secretary, Treasurer and Editor. Professor M. J. Buerger spoke on the desirability of an International Union of Mineralogy. Acting on this suggestion, the 1957 Council appointed a committee to investigate the possibility of organizing such an International Union.

In order not to take time from the scientific sessions, only fifteen minutes have been allotted for the annual business meeting. This is too short a time to discuss items of business that may be brought up by members. To correct this situation, the Council has voted that in the future the business meeting will be held at the end of an afternoon scientific session. Discussion can then be held without time limitations.

The 1956 Council of the Society met for seven hours on October 30 and November 1 and discussed twenty-four items of business. The following are those which the Council feels are of general interest to the membership:

Nomenclature Committee. The report of the Committee was given by George Faust, Chairman. In 1955 the Committee submitted to the Council the results of a survey of the literature regarding the methods used to designate indices of refraction. The 1956 Committee, consisting of six members, voted on their preference. The results of the Committee's voting are as follows:

$$\alpha, \beta, \gamma\text{—3 votes;} \quad n_x\ n_y\ n_z\text{—2 votes;} \quad N_x, N_y, N_z\text{—1 vote}$$

It was voted to accept the report of the Committee. It was further voted that the Nomenclature Committee prepare a brief statement giving the background of the various usages regarding designation of refractive indices that could be circulated to the whole membership of the Society. The members would be asked to express their preference and unless important new points are brought up, the result of this balloting is to be considered a final vote on a system to be adopted officially for use in *The American Mineralogist.*

A sub-committee consisting of Tuttle, Goldsmith and MacKenzie is to prepare a report on the nomenclature of the feldspars.

A sub-committee is working on the nomenclature of the clay minerals.

American Geological Institute. The American Geological Institute is endeavoring to put its finances on a firmer basis by having member organizations, of which the Mineralogical Society of America is one, contribute a percentage of the dues paid by members. The Council voted that the Mineralogical Society of America contribute to the American Geological Institute in 1957 10 per cent of the current dues paid by Members and Fellows with the dues of both considered as $4.00.

On April 23, 1956 there was a meeting of the Government Relations Committee of the American Geological Institute. Our Society representative at the meeting, D. Jerome Fisher, reported that the following items were considered:

1. Mission 66 of Department of Interior to improve National Parks and Monuments.
2. Ways and means of getting geological instruction in U. S. Military Academies.
3. Need for getting essential geological advice into Public Works.
4. How A.G.I. can help the Scientific Manpower Commission.
    a. Drafting of scientists; educational problems of science.
    b. Use of scientists in government research laboratories.
    c. Need to include geologic exploration as research.

International Geological Congress. D. Jerome Fisher, the Mineralogical Society of America representative to the Mexican Congress, reported to the Council on the recent meetings. He suggested that in the future we have more delegates and try to arrange more papers of a mineralogical nature.

Translation of Russian Scientific Publications. The National Science Foundation has undertaken a program of translating Russian publications. The Council felt that mineralogical material should be included and that the best approach to the National Science Foundation would be through the American Geological Institute. Accordingly, the Council voted that the following resolution be transmitted to the American Geological Institute by a Mineralogical Society of America representative: "The Mineralogical Society of America is anxious to see that mineralogical material is included among items translated from the Russian and the Mineralogical Society of America Council will be glad to cooperate in any feasible manner toward this end."

Harvard Supplement. Members of the Harvard Department of Mineralogy requested that they be permitted to prepare papers for and publish a supplement to *The American Mineralogist* during 1957. It is understood that Harvard would assume the complete cost of the supplement and that, separately bound, it would be distributed to all Fellows, Members, and Subscribers of *The American Mineralogist*. It was agreed that the papers should be processed in the same manner as those normally submitted for publication in *The American Mineralogist*. The Council voted to authorize such a supplement.

Decennial Index. Earl Ingerson reported that the manuscript for the Index, prepared under his guidance, has been completed and should be published early in 1957.

The 1957 Council met for three hours on November 1 and discussed the following items of business:

Committee Appointments. President Fisher made various committee appointments which were approved by the Council.

"Permanent Officers". The President felt that there was some feeling among the membership that the length of term of the so-called "permanent" officers of the Society should be considered. Accordingly, he appointed a committee to study the matter and to report to the Council.

Endowment Fund. The President requested information regarding the source of the endowment fund. The Treasurer pointed out that it originated essentially in a single gift from Washington A. Roebling in 1926, and agreed that he would elaborate on sources of funds at the November 1957 Council meeting. The Council discussion of ways and means of increasing the endowment resulted in the appointment of a committee to investigate methods and report to the Council.

System of Mineralogy. The desirability of an appendix to Volume 1 was mentioned. Frondel pointed out that such a work would take considerable time and money as well as competent personnel. He agreed to survey the situation and to determine the cost and length of time necessary to produce a "dry bone" appendix.

Committee Reports. The Council voted that a formal report be requested from the Chairman of each committee to reach the secretary before September 1, 1957.

Mineral Names. The President mentioned the necessity of a rediscussion of the Schaller system of mineral names. It was agreed to refer the matter to the Nomenclature Committee.

COMMITTEES OF THE MINERALOGICAL SOCIETY OF AMERICA FOR 1957

The President wishes to remind the Fellows and Members of their privilege of corresponding with the officers and councilors or any of the personnel of the following committees regarding the business of the Society.

Nominating Committee for Fellows

G. Switzer, *Chairman* 56–58
R. Holmes 55–57
A. W. Jolliffe 56–58
W. R. Foster 57–59
S. E. Clabaugh 57–59

Roebling Medal Committee

A. F. Buddington, *Chairman*
A. J. Frueh, Jr.
J. Verhoogen
C. Frondel

Nominating Committee for Officers

E. N. Cameron, *Chairman*
G. J. Neuerburg
J. E. Hawley
A. C. Waters
D. McConnell

Mineralogical Society of America Award Committee

R. A. Rowland, *Chairman*
G. W. Brindley
C. A. Chapman
L. W. Staples
R. M. Garrels

Nomenclature Committee

C. O. Hutton, *Chairman* 55–57
R. S. Cannon, Jr. 55–57
E. E. Wahlstrom 56–58
H. S. Yoder, Jr. 56–58
H. Winchell 57–59
C. Milton 57–59

Board of Associate Editors

W. F. Bradley 55–57
F. J. Turner 55–57
E. W. Heinrich 56–58
C. L. Christ 56–58
J. Murdock 57–59
R. M. Garrels 57–59

Financial Advisory Committee

E. P. Henderson, *Chairman* 56–58

Auditing Committee

M. D. Foster, *Chairman*
C. A. Anderson
H. L. James

Mineralogical Abstracts Committee

L. G. Berry, *Chairman*
A. Pabst

Constitution Committee

G. E. Goodspeed, *Chairman*
F. Chayes
S. S. Goldich

Program Committee

H. W. Fairbain, *Chairman* 57–59
H. T. Evans 57–59
O. F. Tuttle, 57

Endowment Committee

A. O. Woodford, *Chairman*
C. Frondel
C. B. Slawson

Committee to Study the Length of Officers' Terms

I. Campbell, *Chairman*
T. F. Bates
P. F. Kerr
C. F. Park

Committee to Investigate International Union of Mineralogy

M. J. Buerger, *Chairman*
A. Pabst
S. C. Robinson
J. W. Gruner
J. D. H. Donnay

Corresponding members of the Committee

G. F. Claringbull
H. G. F. Winkler
C. Guillemin

Representatives

A.A.A.S.
C. Tolman 57–59

American Geological Institute

Board of Directors
E. Ingerson 56–57
L. R. Page 57–58

Government Relations Committee
P. F. Kerr 57–58

Glossary Committee
C. Frondel, *Chairman*
E. W. Heinrich
H. R. Gault

National Academy of Sciences National Research Council

J. D. H. Donnay

Committee to set up Criteria for Awards and Medals

R. E. Grim, *Chairman*
G. T. Faust
M. L. Keith
G. C. Kennedy

REPORT OF THE SECRETARY

To the Council of the Mineralogical Society of America:

Election of Officers and Fellows

Five hundred and forty-one ballots were cast in the election of officers, 165 by fellows and 376 by members of the Society. The officers elected to serve in 1957 are:

President: D. Jerome Fisher, University of Chicago, Chicago, Illinois.
Vice-President: G. E. Goodspeed, University of Washington, Seattle 5, Washington.
Secretary: C. S. Hurlbut, Jr., Harvard University, Cambridge 38, Massachusetts.
Treasurer: Earl Ingerson, U. S. Geological Survey, Washington 25, D. C.
Editor: Lewis S. Ramsdell, University of Michigan, Ann Arbor, Michigan.
Councilors (1957–1959): Samuel S. Goldich, University of Minnesota, Minneapolis 14, Minnesota. Brian H. Mason, American Museum of Natural History, New York 24, New York.

According to the provisions of the Constitution, the following have been elected to fellowship:

Peter Gay, University of Cambridge, Cambridge, England.
Arthur Feodor Hagner, University of Illinois, Urbana, Illinois.
Peggy-Kay Hamilton, Columbia University, New York, New York.
Richard Thomas Liddicoat, Jr., Gemological Institute of America, Los Angeles, California.
Helen Dick Megaw, Cavendish Laboratory, Cambridge, England.
Stephen R. Nockolds, University of Cambridge, Cambridge, England.
Stephen Clive Robinson, Geological Survey of Canada, Ottawa, Ontario, Canada.
Joseph Victor Smith, University of Cambridge, Cambridge, England.
Frederick Henry Stewart, University of Durham, Durham, England.
Ada Swineford, State Geological Survey of Kansas, Lawrence, Kansas.
James B. Thompson, Jr., Harvard University, Cambridge, Massachusetts.
Jean Wyart, Faculte des Sciences de Paris, France.

MEMBERSHIP STATISTICS

November 1, 1956

	1955	*1956*	*Gain*	*Loss*
Correspondents	4	4	0	0
Fellows	338	345	12	5
Members	957	1,014	145	88
Subscribers	952	966	70	56
	2,251	2,329	227	149

The above figures show a net gain of 7 fellows, 57 members and 14 subscribers. Considering the four groups, together, there is a gain of 78, giving a total of 2,329.

During 1956, the Society lost through death five fellows: N. L. Bowen, Washington, D. C.; W. F. Foshag, Washington, D. C.; G. H. Anderson, New York, N. Y.; D. Hoenes, Karlsruhe, Germany; F. Pardillo, Barcelona, Spain.

Respectfully submitted,
C. S. HURLBUT, JR., *Secretary*

REPORT OF THE TREASURER FOR 1956

To the Council of the Mineralogical Society of America:

Your Treasurer submits herewith his report for the fiscal year beginning August 1, 1955, and ending July 31, 1956.

RECEIPTS

Dues and subscriptions	$11,957.00
Sale of back numbers	2,306.33
Authors' charges on reprints	1,569.14
Interest and dividends from endowment	5,662.25
Geological Society of America aid for printing the Journal	8,000.00
Advertising	1,175.95
Contributions to Kraus Volume	310.00
Sale of Index, vols. 21–30	14.00
Sale of Index, vols. 1–20	6.00
	$31,000.67
Cash on hand, August 1, 1955	7,747.58
	$38,748.25

DISBURSEMENTS

Printing and distribution of the Journal (6 issues)	$18,228.38
Printing and distribution of reprints	1,546.08
Honoraria to Editor, Secretary, and Treasurer	1,250.00
Clerical assistance	1,143.88
Printing and stationery	477.92
Program and abstracts (1955)	267.04
Roebling Medal (1955)	133.18
Postage and express	766.50
Expenses of officers to 1955 meetings	220.60
New securities purchased	9,047.50
Commission on new securities	89.94
Tax on new securities	1.20
Office equipment	3.29
Safety deposit box	7.15
Refunds	13.51
Telephone and telegrams	1.38
Committee expenses	5.00
Mineralogical Society of America Award certificate	8.00
Contribution to American Geological Institute	100.00
Reprinting back issues	136.53
Expenses in preparation of Index to volumes 31–40	928.81
Mineralogy pamphlet	212.41
Exchange charges on checks	.57
Purchase of back issues	28.00
Check returned	11.00
	$34,627.87
Cash on hand, July 31, 1956	4,120.38
	$38,748.25

The endowment funds of the Society as of July 31, 1956, consist of the following securities:

BONDS

6M Atlantic Coast Line, $4\frac{1}{2}$	$5,257.50	
5M New York Central, 5	4,300.00	
5M Southern Railway, 5	5,743.75	
		$15,301.25

PREFERRED STOCKS

500 Union Pacific, 4	$4,570.25	
200 Southern California Edison, 4.88	5,250.00	
150 Penn-Texas, 1.60	4,487.50	
60 Jones and Laughlin, A, 5	4,987.50	
55 United States Steel, 7	6,946.20	
50 Virginia Electric and Power, 5	5,942.50	
10 Consolidated Edison, 5	1,066.64	
		$33,250.59

Common Stocks

346 Potomac Electric Power	$4,966.73	
200 Columbia Gas	3,200.00	
200 Greyhound Corporation	2,300.00	
168 Standard Oil of New Jersey	1,444.84	
150 Spencer Kellogg	3,775.00	
100 Columbus and Southern Ohio Electric	2,087.50	
100 Diana Stores	1,250.00	
100 Pittsburgh and West Virginia	2,787.50	
80 Kroger Company	1,990.00	
67 American Telephone and Telegraph	9,231.32	
60 United Fruit	3,067.50	
50 Chesapeake and Ohio	2,368.75	
50 Phelps Dodge	1,975.00	
50 Sinclair Oil	2,968.75	
40 Plymouth Cordage	2,050.00	
30 U. S. Playing Card	2,411.25	
24 Public Service Electric and Gas	728.40	
		48,602.54
		$97,154.38

Respectfully submitted,
Earl Ingerson, *Treasurer*

DANA FUND

Available balance, August 1, 1955	$99.25
Disbursements	99.25

Account closed, July 31, 1956.

Respectfully submitted,
Earl Ingerson, *Treasurer*

REPORT OF THE AUDITING COMMITTEE

To the President of the Mineralogical Society of America:

The Auditing Committee has examined and verified the accounts of the Treasurer of the Mineralogical Society of America for the fiscal year beginning August 1, 1955, and ending July 31, 1956. The securities listed in the Treasurer's report, with all future coupons on the coupon bonds attached, are in the safety deposit box at the 17th and G Street Branch of the Riggs National Bank in Washington, D. C.

Respectfully submitted,
Margaret D. Foster
S. Zerfoss
John C. Rabbitt, *Chairman*

REPORT OF THE EDITOR FOR 1956

To the Council of the Mineralogical Society of America:

In order that there might be continuity and direct comparison with reports of previous years, the editor's report for 1956 will follow in general the same plan and procedure of former years. In general, it may be stated that the accomplishments of the year represent what might be termed the work of a normal year. No special issues devoted to specific purposes or individuals were requested. These special issues have in the past increased the annual volume beyond what might be considered the normal size. Also this year, the first time since 1949, our Canadian neighbors have decided to re-establish their own "Contributions to Canadian Mineralogy," which for the past seven years they have shared with us. We wish them success as there appears to be sufficient available material to justify expanding outlets for mineralogical papers. Also it should have the effect of shortening the period of papers held awaiting publication in our own Journal.

The 1956 volume has 981 pages, averaging about 164 pages for each of the six issues, and contains 64 leading articles. Forty-eight additional short papers, appearing under Notes and News, give an over-all total of 112 published manuscripts for the year. These contributions were received from 144 contributors associated with 57 different universities, research bureaus and technical laboratories. Thirty critical book reviews and six new minerals described in detail for the first time are a few of the other items of special mineralogical interest. Also in the current volume under the heading of New Mineral Names, which includes discredited species and new data, Dr. Fleischer has critically evaluated for our readers 70 mineral names that have been introduced into our literature. As a matter of permanent record, recognition and deep appreciation is here expressed for the valiant service performed by Dr. Fleischer who for the past 16 years has had charge of this section of the Journal. His critical remarks and sound judgment in evaluating the propriety of proposed new mineral names has been of inestimable service.

As in previous years our service during 1956 has extended far beyond our own borders. During the current year 21 manuscripts came from 11 countries: Australia, Brazil, Canada, England, Finland, India, Japan, Netherlands, New Zealand, South Africa and Switzerland.

As in former years the Geological Society of America has continued its liberal financial support defraying a very substantial portion of the printing costs of the Journal. For this timely assistance, with the printing costs on the up-grade, the Society is indeed very grateful and expresses its deep appreciation.

And now a word as to the prospects for 1957. The January-February manuscripts containing 10 main articles and 6 shorter papers are in the hands of the printer at present. In addition at the present time there are on file only a total of 25 papers, aggregating about 330 typed pages, so that substantial progress has been achieved in decreasing the heavy back-log that has caused considerable concern in the past. Instead of about a year that has been required in the past between receipt of material and publication, the interval has been reduced to approximately 8 months. I am sure this is gratifying news to authors and readers alike. I am hopeful that by continuing rigid inspection and stressing condensation as far as practical this record may be continued and the time interval possibly slightly reduced.

Data summarizing the distribution of subject matter in volume 41 are given in Table 1.

In conclusion, in making my report for the last time, after a service as your editor for 35 years, may I take this opportunity to express to the Council, past and present, to the contributors and to our members my thanks for their loyal support and cooperation. Whatever progress has been attained during this period is not due to the work of any single individual but to the joint efforts of all who have shared in this undertaking.

My successor, Professor Lewis S. Ramsdell, has been an assistant editor since 1952 and has been my co-worker on the Journal for a number of years prior to that date. He is experienced and will bring no doubt new suggestions for the further improvement of the Journal. I am sure he will continue to receive the cordial and hearty cooperation that you have so graciously extended to me in the past.

Respectfully submitted
WALTER F. HUNT, *Editor*

Table 1. Distribution of Subject Matter in Volume 41

Subjects	Articles	Pages	Per Cent of Total
Leading articles*			
Descriptive mineralogy and paragenesis	13		
Chemical mineralogy and geochemistry	16		
Structural crystallography	17		
Geometrical crystallography	2		
Petrography	3		
Optical crystallography	4		
Memorials	5		
Miscellaneous	4		
	64	734	75.4
Short articles—Notes	48	$129\frac{1}{2}$	24.6
News	27	$5\frac{1}{2}$	
Proceedings of Society	1	45	
Book reviews	30	24	
Abstracts of new mineral names	70	22	
Total entries	240	960	100.0
Illustrations	244		
Index, Title page, Table of contents		21	
Grand total		981	

* Leading articles average 11.5 printed pages.

LIST OF FORMER OFFICERS AND MEETING PLACES

By recommendation of the Council, a complete list of past officers is printed in the proceedings of the annual meeting of the Society:

Honorary Presidents

Edward S. Dana 1925–1935
Charles Palache 1949–1954
Edward H. Kraus 1955–

Presidents

1920 Edward H. Kraus
1921 Charles Palache
1922 Thomas L. Walker
1923 Edgar T. Wherry
1924 Henry S. Washington
1925 Arthur S. Eakle
1926 Waldemar T. Schaller
1927 Austin F. Rogers
1928 Esper S. Larsen
1929 Arthur L. Parsons
1930 Herbert E. Merwin
1931 Alexander H. Phillips
1932 Alexander N. Winchell
1933 Herbert P. Whitlock
1934 John W. Wolff
1935 Clarence S. Ross
1936 William S. Bayley
1937 Norman L. Bowen
1938 Ellis Thomson
1939 Max N. Short
1940 William F. Foshag
1941 Frederick E. Wright
1942 Arthur F. Buddington
1943 John F. Schairer
1944 R. C. Emmons

1945 Kenneth K. Landes
1946 Paul F. Kerr
1947 M. J. Buerger
1948 M. A. Peacock
1949 John W. Gruner
1950 George Tunell
1951 A. Pabst
1952 Michael Fleischer
1953 J. D. H. Donnay
1954 Sterling B. Hendricks
1955 Harry H. Hess
1956 Clifford Frondel

Secretaries

1920–1922 Herbert P. Whitlock
1923–1933 Frank R. Van Horn
1933–1934 Albert B. Peck
1934–1944 Paul F. Kerr
1944– C. S. Hurlbut, Jr.

Vice-Presidents

1920 Thomas L. Walker
1921 Waldemar T. Schaller
1922 Frederick A. Canfield
1923 George F. Kunz
1924 Washington A. Roebling
1925 Herbert P. Whitlock
1926 George Vaux, Jr.
1927 George L. English
1928 Lazard Cahn
1929 Edward Wigglesworth
1930 John E. Wolff
1931 William F. Foshag
1932 Joseph L. Gillson
1933 Frank B. Guild
1934 William A. Tarr
1935 Ellis Thomson
1936 Harold L. Alling
1937 H. V. Ellsworth
1938 Kenneth K. Landes
1939 Burnham S. Colburn
1940 Ian Campbell
1941 William J. McCaughey
1942 Martin J. Buerger
1943 John W. Gruner
1944 Harry Berman
1945 George Tunell
1946 S. B. Hendricks
1947 Carl Tolman
1948 Adolf Pabst
1949 J. D. H. Donnay
1950 Ralph E. Grim
1951 Michael Fleischer
1952 J. D. H. Donnay
1953 Sterling B. Hendricks
1954 Harry H. Hess
1955 Clifford Frondel
1956 D. Jerome Fisher

Treasurers

1920–1923 Albert B. Peck
1924–1929 Alexander H. Phillips
1929–1930 Albert B. Peck
1930–1940 Waldemar T. Schaller
1941– Earl Ingerson

Editors

1920–1921 Edgar T. Wherry
1922–1956 Walter F. Hunt

Councilors

1920 Arthur S. Eakle, Frank R. Van Horn, Fred E. Wright, Alexander H. Phillips.
1921 Frank R. Van Horn, Fred E. Wright, Alexander H. Phillips, Austin F. Rogers.
1922 Fred E. Wright, Alexander H. Phillips, Austin F. Rogers, Thomas L. Watson.
1923 Alexander H. Phillips, Austin F. Rogers, Thomas L. Watson, Esper S. Larsen.
1924 Austin F. Rogers, Thomas L. Watson, Esper S. Larsen, Arthur L. Parsons.
1925 Thomas L. Watson, Esper S. Larsen, Arthur L. Parsons, William F. Foshag.
1926 Esper S. Larsen, Arthur L. Parsons, William F. Foshag, William A. Tarr.
1927 Arthur L. Parsons, William F. Foshag, William A. Tarr, Alexander N. Winchell.
1928 William F. Foshag, William A. Tarr, Alexander N. Winchell, Ellis Thomson.
1929 William A. Tarr, Alexander N. Winchell, Ellis Thomson, Clarence S. Ross.

1930 Alexander N. Winchell, Ellis Thomson, Clarence S. Ross, Paul F. Kerr.
1931 Ellis Thomson, Clarence S. Ross, Paul F. Kerr, William S. Bayley.
1932 Clarence S. Ross, Paul F. Kerr, William S. Bayley, William J. McCaughey.
1933 Paul F. Kerr, Wiliam S. Bayley, William J. McCaughey, Kenneth K. Landes.
1934 William S. Bayley, William J. McCaughey, Kenneth K. Landes, E. P. Henderson.
1935 William J. McCaughey, Kenneth K. Landes, E. P. Henderson, J. F. Schairer.
1936 Kenneth K. Landes, E. P. Henderson, J. F. Schairer, Arthur F. Buddington.
1937 E. P. Henderson, J. F. Schairer, Arthur F. Buddington, Arthur P. Honess.
1938 J. F. Schairer, Arthur F. Buddington, Arthur P. Honess, R. C. Emmons.
1939 Arthur F. Buddington, Arthur P. Honess, R. C. Emmons, Carl Tolman.
1940 Arthur P. Honess, R. C. Emmons, Carl Tolman, D. Jerome Fisher.
1941 R. C. Emmons, Carl Tolman, D. Jerome Fisher, Martin A. Peacock.
1942 Carl Tolman, D. Jerome Fisher, Martin A. Peacock, Adolf Pabst.
1943 D. Jerome Fisher, Martin A. Peacock, Adolf Pabst, C. S. Hurlbut, Jr.
1944 Martin A. Peacock, Adolf Pabst, Michael Fleischer, S. J. Shand.
1945 Adolf Pabst, Michael Fleischer, S. J. Shand, R. E. Grim
1946 Michael Fleischer, S. J. Shand, R. E. Grim, Joseph Murdoch.
1947 S. J. Shand, R. E. Grim, Joseph Murdoch, H. H. Hess.
1948 R. E. Grim, Joseph Murdoch, H. H. Hess, Clifford Frondel.
1949 Joseph Murdoch, H. H. Hess, Clifford Frondel, Lewis S. Ramsdell.
1950 H. H. Hess, Clifford Frondel, Lewis S. Ramsdell, E. F. Osborn.
1951 Clifford Frondel, Lewis S. Ramsdell, E. F. Osborn, George T. Faust.
1952 Lewis S. Ramsdell, E. F. Osborn, George T. Faust, Victor T. Allen.
1953 E. F. Osborn, George T. Faust, Victor T. Allen, C. Osborne Hutton.
1954 George T. Faust, Victor T. Allen, C. Osborne Hutton, Felix Chayes
1955 Victor T. Allen, C. Osborne Hutton, Felix Chayes, L. G. Berry.
1956 C. Osborne Hutton, Felix Chayes, L. G. Berry, C. B. Slawson, A. O. Woodford.

Annual Meeting Places

1920 Chicago, Illinois
1921 Amherst, Massachusetts
1922 Ann Arbor, Michigan
1923 Washington, D. C.
1924 Ithaca, New York
1925 New Haven, Connecticut
1926 Madison, Wisconsin
1927 Cleveland, Ohio
1928 New York, N. Y.
1929 Washington, D. C.
1930 Toronto, Canada
1931 Tulsa, Oklahoma
1932 Cambridge, Massachusetts
1933 Chicago, Illinois
1934 Rochester, New York
1935 New York, N. Y.
1936 Cincinnati, Ohio
1937 Washington, D. C.
1938 New York, N. Y.
1939 Minneapolis, Minnesota
1940 Austin, Texas
1941 Boston, Massachusetts
1942 No meeting held
1943 No meeting held
1944 No meeting held
1945 Pittsburgh, Pennsylvania
1946 Chicago, Illinois
1947 Ottawa, Canada
1948 New York, N. Y.
1949 El Paso, Texas
1950 Washington, D. C.
1951 Detroit, Michigan
1952 Boston, Massachusetts
1953 Toronto, Canada
1954 Los Angeles, California
1955 New Orleans, Louisiana
1956 Minneapolis, Minnesota

Recipients of the Roebling Medal

Charles Palache, December 1937
Waldemar T. Schaller, December 1938
Leonard James Spencer, December 1940
Esper S. Larsen, Jr., December 1941
Edward H. Kraus, February 1945
Clarence S. Ross, December 1946
Paul Niggli, December 1947
William Lawrence Bragg, November 1948
Herbert E. Merwin, November 1949
Norman L. Bowen, November 1950
Fred E. Wright, November 1952
William F. Foshag, November 1953
Cecil Edgar Tilley, November 1954
Alexander N. Winchell, November 1955
Arthur F. Buddington, November 1956

Recipients of the Mineralogical Society of America Award

Orville Frank Tuttle, November 1951
Frederick H. Stewart, November 1952
L. H. Ahrens, November 1953
Hatten S. Yoder, Jr., November 1954
Julian R. Goldsmith, November 1955
George C. Kennedy, November 1956

1956 ANNUAL MEETINGS AT MINNEAPOLIS, MINNESOTA

The meetings of the following Societies were held on Oct. 31, Nov. 1, 2, 1956.

The Geological Society of America—69th
The Paleontological Society—48th
The Mineralogical Society of America—37th
Society of Economic Geologists—37th
Society of Vertebrate Paleontology—16th
Association of Geology Teachers
Geochemical Society

The complete program listed titles and abstracts of 193 papers. Of these 91 seemed to be of special interest to members of The Mineralogical Society of America. Authors and titles of these papers are listed below. Since by Council action the abstracts will not be reprinted in *The American Mineralogist*, references are given to the *Bulletin of the Geological Society of America*, Vol. 67, Number 12, Part 2, December 1956, pp. 1663–1747 where the abstracts of all the papers of the various societies are reprinted, arranged alphabetically by authors.

Papers of Special Mineralogical Interest

John A. S. Adams and Richard Pliler: *Geochemistry of the actinides as a possible clue in interpreting the development of the earth's atmosphere.* Page 1663.

Gilles Allard: *Dore Lake complex, petrography and metamorphism.* Page 1663.

Victor T. Allen and Joseph J. Fahey: *Actinolite at Iron Mountain, Missouri.* Page 1664.

Lloyd L. Ames, Jr., L. B. Sand, and S. S. Goldich: *Contribution on the Hector, California bentonite deposit.* Page 1665.

Daniel Appleman: *Crystal structure of liebigite.* Page 1666.

R. G. Arnold: *Subsolidus relations in the system* $FeS\text{-}FeS_2$. Page 1667.

Paul B. Barton, Jr. *Limitations on the possible composition of the ore-forming fluid.* Page 1668.

Thomas F. Bates and Erwin O. Strahl: *Regional study of the mineralogy and petrology of the Chattanooga shale.* Page 1669.

Gordon D. Bath and George M. Schwartz: *Regional aeromagnetic study of the Mesabi district, Minnesota.* Page 1669.

Kenneth O. Bennington: *Differentiation due to shearing.* Page 1669.

Philip M. Bethke: *Sulfo-selenides of mercury*. Page 1671.

Barrie H. Bieler and Harold D. Wright: *Relationship of vein color to minor-element content of some uranium-bearing "siliceous reef" veins in the Boulder batholith, Montana*. Page 1672.

Marc W. Bodine, Jr., and Paul F. Kerr: *Hydrothermal dolomitization of sandstone, Temple Mountain, Utah*. Page 1673.

F. R. Boyd and J. L. England: *Breakdown of nepheline under pressure*. Page 1674.

M. J. Buerger: *Crystal structure of pectolite and wollastonite*. Page 1677.

Wayne M. Bundy and Robert F. Conley: *Gypsification via transient double salts*. Page 1677.

John F. Burst: *Mineralogic variability in glauconitelike pellets and its application in stratigraphic studies*. Page 1678.

Alfred L. Bush: *Vanadium-uranium deposits in the Entrada sandstone, western San Juan Mountains, Colorado*. Page 1678.

Eugene N. Cameron and Harry E. Abendroth: *Occurrence of chromite deposits in the eastern part of the Bushveld complex*. Page 1678.

C. L. Christ and Joan R. Clark: *Crystal structure of meyerhofferite*, $2CaO \cdot 3B_2O_3 \cdot 7H_2O$. Page 1680.

Joan R. Clark and C. L. Christ: *Ammonioborite and larderellite*. Page 1680.

R. F. Cormier, L. F. Herzog, W. H. Pinson and P. M. Hurley: *Rubidium-strontium age determinations on the mineral glauconite*. Page 1681.

Frank Dachille and Rustum Roy: *System* Mg_2SiO_4—Mg_2GeO_4 *at* 10,000, 60,000, *and about* 300,000 psi. Page 1682.

Paul E. Damon and Philip A. Kluft: *Further investigations of excess helium and argon in minerals and rocks*. Page 1683.

E. C. Dapples: *Grades of diagenesis in sandstones*. Page 1684.

Edward S. Davidson: *Rainy Day uranium deposit, Garfield County, Utah*. Page 1685.

Reynolds M. Denning: *Grinding hardness of diamond in a principle cutting direction*. Page 1686.

Maurice Deul: *Concentration of minor elements in carbonaceous fractions mechanically segregated from some sedimentary rocks*. Page 1686.

George W. DeVore: *Effect of some strong-weak cation associations on the distribution of* Mg *and* Fe^{2+} *in coexisting minerals*. Page 1687.

F. Donald Eckelmann, J. Laurence Kulp, and John S. Brown: *Lead isotopes and the pattern of mineralization in southwest Missouri*. Page 1689.

Walter R. Eckelmann and James C. Cobb: *Discordant uranium-lead ages and mineral type*. Page 1690.

R. C. Emmons and J. B. Jones: *Chelation, a possible geologic process*. Page 1692.

A. E. J. Engel and Celeste G. Engel: *Distribution of copper, lead, and zinc in hydrothermal dolomites associated with sulfide ore in the Leadville limestone (Mississippian, Colorado)*. Page 1692.

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Howard T. Evans, Jr. and Mary E. Mrose: *Crystal chemical studies of low-valence vanadium oxide minerals from the Colorado Plateau*. Page 1693.

Howard T. Evans, Jr. and Mary E. Mrose: *Crystal chemistry of duttonite*. Page 1693.

D. Jerome Fisher: *Hagendorfite unit cell*. Page 1694.

D. Jerome Fisher: *Isokite from a Bohemian pegmatite*. Page 1695.

Margaret D. Foster: *Layer-charge relationships of the muscovite and biotite micas*. Page 1696.

Gerald M. Friedman: *Progress report on the Mamainse "diabase," Algoma district, Ontario, Canada*. Page 1697.

Alfred J. Frueh, Jr.: *Crystal structure of eucairite.* Page 1697.

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Julian R. Goldsmith: *Exsolution of dolomite from calcite.* Page 1699.

Félix González-Bonorino: *Hydrothermal alteration in tungsten and gold-pyrite veins of Boulder County, Colorado.* Page 1699.

David Gottfried, C. L. Waring, and H. W. Worthing: *Hafnium content, hafnium to zirconium ratio, and radioactivity of zircon from igneous rocks.* Page 1700.

John W. Gruner: *Concentration of uranium in sediments by multiple migration-accretion.* Page 1702.

H. S. Gutowsky and D. M. Henderson: *Structural studies of minerals by means of nuclear magnetic resonance.* Page 1703.

E. Wm. Heinrich and A. A. Giardini: *Radioactive columbite-tantalite.* Page 1704.

D. M. Henderson and H. S. Gutowsky: *Nuclear magnetic resonance determination of the position of hydrogen in* $Ca(OH)_2$*—portlandite.* Page 1705.

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John C. Jamieson: *Polymorphism at high hydrostatic pressure.* Page 1710.

George C. Kennedy: *Polymorphism in the feldspars at high temperature and pressures.* Page 1711.

J. L. Kulp, W. U. Ault, and D. S. Miller: *Relation of lead and sulfur isotopes to the origin of Mississippi Valley ores.* Page 1713.

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John Lemish: *Hydrothermal alteration of the Topia mining district, Durango, Mexico.* Page 1715.

L. A. Long and J. L. Kulp: *Potassium-argon ages from the New York City and Spruce Pine, North Carolina areas.* Page 1716.

D. Keith Lupton: *Soda-rich igneous rocks of Hell's Canyon, Idaho.* Page 1717.

A. J. Majumdar and Rustum Roy: *Limitations on calculations, relating p-t equilibria to thermochemically determined parameters.* Page 1718.

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Harold Masursky: *Uranium-bearing coal in the Red Desert, Wyoming.* Page 1719.

George W. Morey: *Action of hot water on some carbonates.* Page 1721.

Frederick A Mumpton and Rustum Roy: *Hydrothermal study of some hydrous copper silicates.* Page 1722.

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Bartholomew Nagy: *Structure of* (O)—H—O—H *units associated with kaolinite deduced from infrared vibrational spectra.* Page 1722.

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William F. Read: *Evolution of corrosion zones in limestone and dolomite.* Page 1726.

J. H. Remick: *Stratigraphy and petrography of the iron formation at Ross Mountain, Quebec* Page 1727.

C. Robbins and F. Chayes: *Compositions of feldspars in some two-feldspar granites.* Page 1727.

John J. W. Rogers and John A. S. Adams: *Distribution of alpha-emitting elements in the volcanic rocks of Mount Lassen, California.* Page 1728.

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Rustum Roy: *New data bearing on the crystal chemistry of the silica polymorphs.* Page 1730.

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A. Van Valkenburg and G. Rynders: *Synthesis of cuspidine,* $3CaO \cdot 2SiO_2 \cdot CaF_2$. Page 1740.

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H. D. Wright and W. P. Shulhof: *Uranium content of base-metal sulfide minerals as an indication of the uranium concentration in ore-forming solutions.* Page 1745.

H. S. Yoder and C. E. Tilley: *Natural tholeiite basalt—water system.* Page 1746.

NOTES AND NEWS

A MODIFIED HULL-DAVEY CHART FOR HIGH VALUES OF *c/a*

Cecil J. Schneer, *Department of Geology and Geography, University of New Hampshire, Durham, New Hampshire*

In the course of recent syntheses of iron oxides (Holser and Schneer, 1953) and an investigation of polymorphism in one dimension (Schneer, 1953), the routine identification of multi-layer polymorphs in powder photographs became necessary. Published charts of the Hull-Davey (1921) type extend only to *c/a* (5.4), (Fairbanks, 1928, or Davey, 1934).[1] A new chart, Fig. 1, was constructed for trigonal and hexagonal spacings covering *c/a* ratios from 3 to 18, corresponding to unit cell heights in close-packed structures of 4 to 21 layers. After the method of Owen and Preston (1923; *Cf.* Ewald, 1923; Harrington, 1938), ordinates were plotted on a logarithmic scale. The curves were plotted from approximately 1,000 spacings. Lines for (*hhl*), *l* not divisible by 3 or 2, were omitted. The omitted spacings occur only if there are no glide planes as in Davey's (1934) "simple triangular lattice." This symmetry occurs in close-packed structures only for randomly stacked layers, in which event there is only one layer per unit cell and the previously published charts may be used. Non-close-packed structures with random layer stacking are not likely to exceed the limit of Davey's chart.

Bravais-Miller indices (*hkil*) with *i* omitted are employed throughout.

Use of the Chart

Recapitulating Hull and Davey (1921), a strip of paper is placed along the horizontal scale. The *d* spacings of the unknown, as determined from a powder photograph, are marked on the strip against the scale. If the composition of the mineral is known and the structure is close-packed, the (100) spacing equals $\sqrt{3}\times$(anion radius). The strip is placed with this spacing on the vertical (100) line of the chart, and moved vertically over the chart until all of the marks on the strip simultaneously intersect lines on the chart. Indices and *c/a* are read directly. If the layer height of a unit cell is within the range 4 to 21 and the structure is close-packed, the marks should meet lines at an integral layer height. If the (100) spacing is not known in advance, the strip must be slid back and forth horizontally as well as vertically in search of a match position.

Because of the characteristic syntaxic intergrowth of layer poly-

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[1] An unpublished chart by A. E. Austin, Battelle Memorial Institute, extends to *c/a* (10), and a chart by R. E. Riley and W. Rostocker, Armour Foundation, extends to *c/a* (2.7).

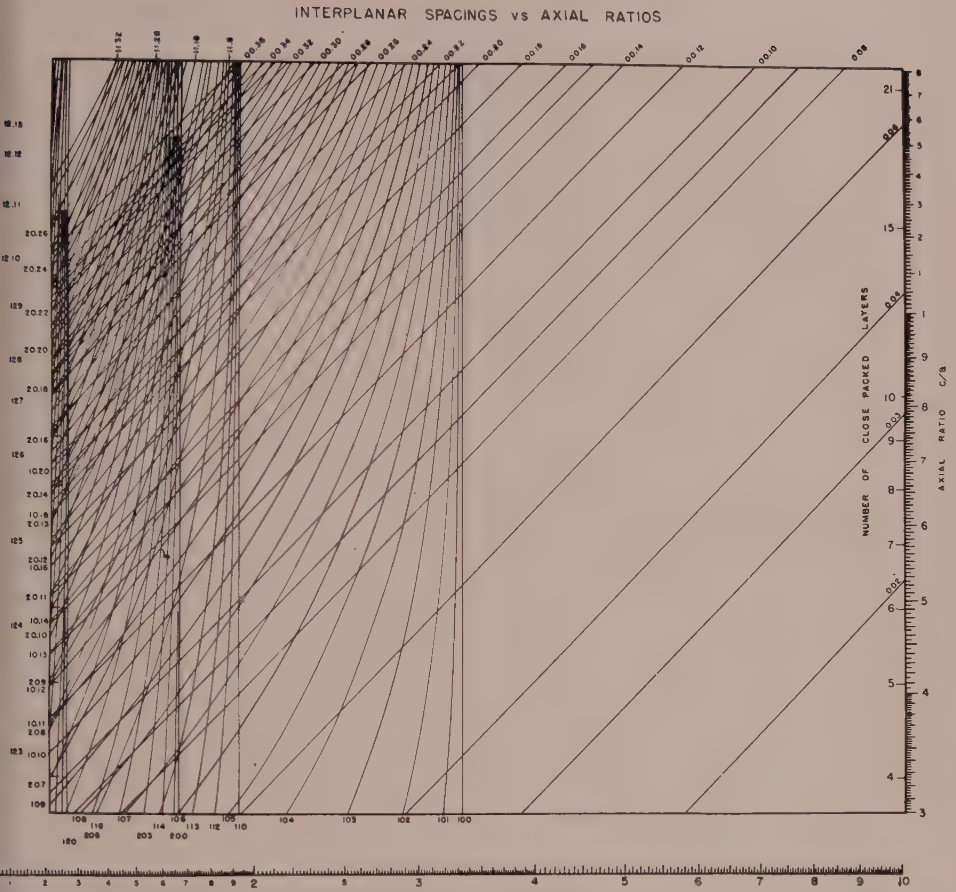

FIG. 1. Chart for high values of c/a.

morphs (Mitchell, 1953) and the increase in the density of lines with increase in the number of layers, a powder photograph of a syntaxic intergrowth of small layer height polymorphs might be difficult to interpret. The characteristic close-in lines of high spacings are lost in the central blind region of the Straumanis film. For these reasons, the chart is chiefly useful in detecting polymorphic changes in the course of thermal treatment of powder samples. Like the powder method itself, results may be statistical, with all of the advantages and disadvantages that go with an averaging procedure.

EXAMPLES

Figure 2 illustrates data from three separate powder patterns, representing three compounds which are chemically distinct but struc-

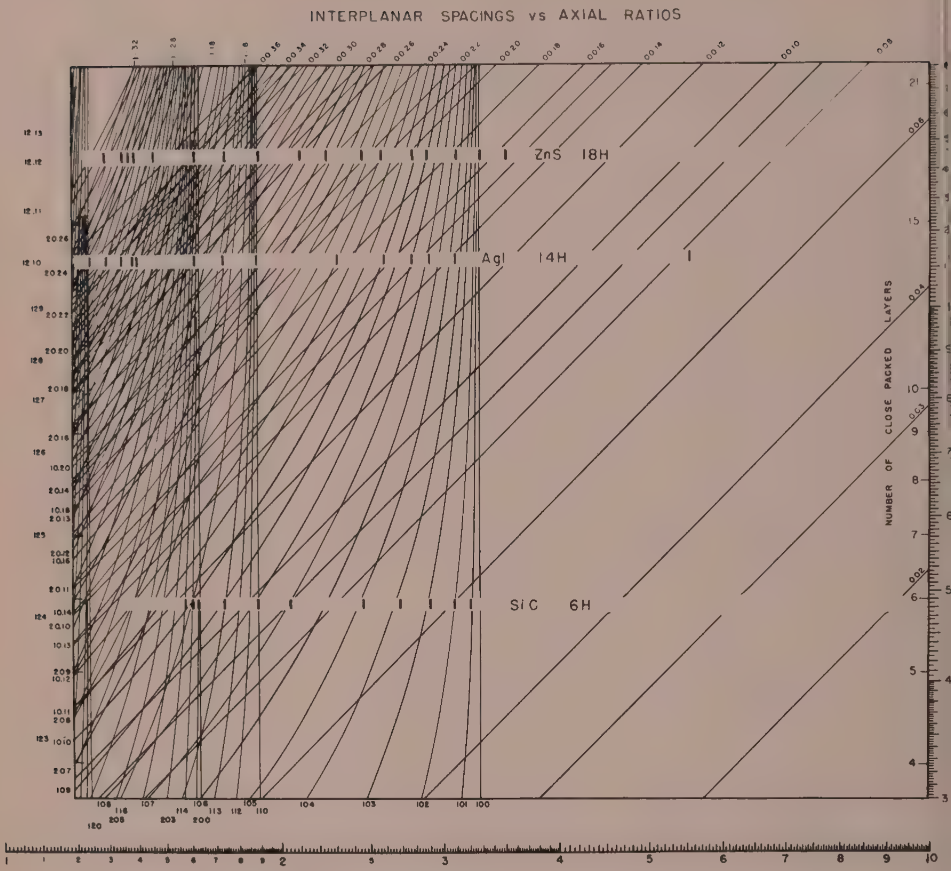

Fig. 2. Examples. Plots of observed spacings from powder photographs of SiC (6H) after Thibault, ZnS (18H?), and AgI (14H?).

turally uniform. The lower strip is SiC (6H). Spacings are as observed by Thibault (1944). The graph was constructed primarily to identify spacings in multi-layer polymorphs in a series of experiments now in progress on the thermodynamics of polymorphism in one dimension. Multilayer polymorphs are interpreted as intermediate stages in the course of second order transformations of the sphalerite-wurtzite type (Schneer, 1955). The upper strip of spacings are from the diffraction pattern of ZnS sublimate at 600° C. While the pattern is incomplete, the lowest position on the graph at which coincidence of lines may be obtained is at c/a 14.720, which is the ratio for ideally packed layers of an 18 layer polymorph. The central strip, even less complete, nevertheless contains lines which can be matched first at c/a 11.445 which is the ratio for ideally packed layers of a 14 layer polymorph. The compound represented by the central strip is AgI held for 24 hours at 120° C. and quenched to room temperature. The experimental work referred to above is now centered on AgI as offering a weakened model structure on which to test the theory of polymorphism in one dimension. Experiment to date has indicated that thermally treated powders yield faint but unmistakable lines on powder diffraction photographs in addition to those identifiable as characteristic of the sphalerite and wurtzite structures. These lines may be indexed graphically as illustrated above. The occurrence of one dimensional polymorphism or *polytypy* in AgI was anticipated by the theory.

Acknowledgments

The graph was begun at the suggestion of Dr. William T. Holser whose encouragment and assistance are reflected throughout this paper. Some of the computations were paid for by the Office of Naval Research. Mr. John Pollock of the University of New Hampshire Engineering Experiment Station, traced the graph. Mr. Auguste Planchon, of the University of New Hampshire, assisted with the AgI research. R. C. Lesser of the Cornell Computing Center, Cornell University, supplied the majority of the computations.

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TRI-KALSILITE, A NEW MINERAL

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This note records the discovery of yet another mineral of composition $(Na,K)AlSiO_4$. The properties of the other phases in the nepheline-kalsilite system have been collected by Smith and Tuttle (1956). The newly-discovered order-disorder in kalsilite is recorded in the following note.

In addition to crystals of kalsilite-nepheline microperthite, the lava from Kabfumu, North Kivu in Belgian Congo, contains parallel growths of a new mineral, tri-kalsilite, and nepheline. After heating to 1000° C. for two hours, one crystal consisted almost entirely of tri-kalsilite. Weak, slightly diffuse reflections revealed the presence of nepheline in parallel association. Tri-kalsilite is hexagonal with *a* 15.4 Å, *c* 8.6 Å, space-group probably $P6_3$. Along with *d*-kalsilite (*a* 5.15 Å), nepheline (*a* 10 Å) and tetra-kalsilite (*a* 20 Å), tri-kalsilite (*a* 15.4 Å) is geometrically related to high-tridymite (*a* 5.0 Å). The structures of kalsilite and nepheline have been shown to be based on a tridymite-type framework of Si, Al tetrahedra and the geometrical and mineralogical relations make it certain that tetra-kalsilite and tri-kalsilite are also based on this type of framework. Tuttle and Smith (in preparation) have shown that just above the nepheline-kalsilite unmixing solvus, nepheline is stable from $Ne_{100}Ks_0$ to $Ne_{30}Ks_{70}$ whereas kalsilite is stable from Ne_0Ks_{100} to $Ne_{20}Ks_{80}$. The tetra-kalsilite phase is produced in charges of composition $Ne_{20}Ks_{80}$ to $Ne_{37}Ks_{63}$ and it is likely that tri-kalsilite occurs in a similar composition range. That these two phases only occur for compositions near the boundary between the stability fields for nepheline and for kalsilite suggests that they are formed metastably, for it is well-known that metastable phases occur readily near phase boundaries.

The close similarity of the optical properties of the tridymite-type phases in the nepheline-kalsilite system renders impracticable a determination of tri-kalsilite by optical methods. The form of occurrence has made it impossible so far to obtain a powder pattern of tri-kalsilite uncontaminated by other phases.

The name tri-kalsilite has, of course, been assigned on the basis of the length of the *a*-axis.

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SMITH, J. V., AND TUTTLE, O. F. (1956), The nepheline-kalsilite system: I. *X*-ray data for the crystalline phases: *Am. Jour. Sci.*, in press.

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ORDER-DISORDER IN KALSILITE

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Kalsilite, the stable form of $KAlSiO_4$ at ordinary temperatures (Tuttle and Smith, in preparation), was first recognized by Holmes (1942) in volcanic rocks from S. W. Uganda. Bannister and Hey (1942), from single-crystal *x*-ray photographs, found that it contained $2KAlSiO_4$ in a hexagonal cell with a 5.17 Å and c 8.67 Å and space-group $P6_32$. Claringbull and Bannister (1948) established that the structure type of kalsilite is $H2_8$ (Gottfried, 1940) but kalsilite can truly belong to this structure type only if the Si and Al atoms are disordered, as was implicitly recognized in the paper. If the Si and Al atoms are ordered, they cannot lie in the same set of positions as is required by the $H2_8$ structure and the true unit-cell must be either larger or less symmetrical. Unfortunately the intensity differences between the ordered and disordered structures would be small and crystals of kalsilite previously found have been too small to provide *x*-ray photographs of sufficient intensity to test whether the Si and Al atoms are ordered.

Recently larger crystals have become available from a lava flow at Kabfumu, Nyiragongo area in North Kivu, Belgian Congo, which has been studied by the second author. The kalsilite occurs as the dominant phase in a kalsilite-nepheline microperthite of a texture similar to that described by Sahama (1953). Careful study of this material by single-crystal *x*-ray methods has revealed very weak, diffuse reflections in addition to the strong, sharp reflections expected for kalsilite and nepheline. The diffuse reflections originate from the kalsilite and show that a new unit-cell must be taken at 30° to the usual 5 Å cell, thus increasing the a repeat distance by $\sqrt{3}$. The c-axis is unchanged and the symmetry remains hexagonal. The space-group appears to be $P6_32$ but little reliance can be placed on it for only the following diffuse reflections have been observed: $(12\bar{3}0)$, $(13\bar{4}0)$, $(24\bar{6}0)$, $(15\bar{6}0)$, $(23\bar{5}1)$ and $(12\bar{3}2)$.

Careful comparison of the photographs obtained for several crystals from the Kabfumu lava revealed variations in the intensity of the diffuse reflections. After heating a crystal at 600° C. for 3 days, the diffuse reflections disappeared giving a kalsilite whose true a repeat was 5.15 Å. Although final proof must await structure-factor calculations it may be concluded that the diffuse reflections are caused by the ordering of Si and Al atoms. Variation in the intensity of the reflections indicates the existence of partial order, thus showing that the kalsilite of the Kabfumu lava has not reached equilibrium.

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So far no other specimens have been investigated, that contain crystals large enough to permit the detection of such weak reflections. As the reflections are too weak for observance on powder photographs, it has not been possible to establish the frequency of occurrence of the two types of kalsilite.

Kalsilite joins the feldspar group of minerals in showing order-disorder of the Al and Si atoms and it is to be expected that further investigation of other minerals that carry Al and Si in four-fold coordination, such as nepheline, will reveal the occurrence of order-disorder. The prefixes *d*- and *o*- are suggested for the characterization of the disordered (*a* 5.15 Å) and ordered (*a* 8.9 Å) forms of kalsilite.

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IDENTITY OF NOCERITE AND FLUOBORITE

Cesare Brisi* and Wilhelm Eitel, *Institute of Silicate Research, University of Toledo, Toledo 6, Ohio*

During an extensive investigation of the silicates and fluorides of calcium and magnesium performed in this Institute, we had the occasion to attempt the synthesis of a compound of the composition $Mg_3Ca_3O_2F_8$, which has been ascribed to the mineral nocerite. In the literature this rare mineral is described from only one occurrence in Nocera, Italy. It is found in volcanic tuffs, in geodes with abundant fluorite, and highly metamorphic inclusions of limestones which are locally dolomitic. Nocerite was described in these typical "piperno" tuffs for the first time by A. Scacchi (1), and repeatedly examined by other mineralogists (cf. Dana's "System of Mineralogy," 7th edition, vol. II. 1944, 1951, pp. 85 f.) Nocerite is hexagonal and is optically negative, with the refractive indices $\omega(Na)=1.5098$, and $\epsilon(Na)=1.4855$ (cf. F. Zambonini (2)); or $\omega=1.512$; $\epsilon=1.487$ (cf. E. S. Larsen (3)).

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Crystals of nocerite were subjected to an accurate *x*-ray examination by A. Scherillo (4). The most probable space groups were determined to be *C*6, or *C*6/*m*. The elementary cell constants are $a_0=8.84$ kX; $c_0=3.12$ kX. In view of the small amount of available pure crystal material, Scherillo was not able to make a complete chemical analysis. However, he discussed the evident difficulties in attempting to bring the formula usually ascribed to nocerite into harmony with the atomic groupings which should be postulated by the space groups indicated above.

All our attempts to synthesize a compound corresponding to the formula $Mg_3Ca_3O_2F_8$ have been in vain. In every case we only obtained mechanical mixtures of MgO, MgF_2, and CaF_2. No more successful were experiments in which were added small amounts of sodium compounds, which, according to some of the chemical analyses reported for nocerite, would make up one of the minor constituents of nocerite.

We then examined the behaviour upon heating of a sample of natural nocerite in order to study the kinetics of its supposed decomposition to the simple oxides and fluorides which are its constituents. The natural material of nocerite* is intimately intergrown with fluorite as shown by a microscopic inspection. Even with heavy liquids and centrifuging we have not been able to eliminate entirely the fluorite from our samples. Therefore, in the *x*-ray powder photographs the lines of CaF_2 are always distinctly identified. The mineral mixture of nocerite with some fluorite is thermally stable when heated for periods of thirty minutes each, at temperatures gradually increased from 300° to 900° C. When the temperature was raised in a closed platinum container to 1000° C., a partial fusion was observed, but the optical and *x*-ray characteristics of the resolidified material are identical with those of the initial mineral. The same results were obtained even by heating at the same temperature over night.

On the other hand, if the thermal exposure to about 900° was prolongated over several days, in an open platinum container, a progressively increasing loss in weight was observed which is accompanied by an irreversible, and finally complete chemical change. The *x*-ray powder patterns of the products treated in this manner show a gradual disappearance of the lines of nocerite and calcium fluoride, giving rise to entirely new lines with increasing intensities. After a sufficiently long exposure nothing of the initial minerals is preserved, and the examination of the new pattern gives the clear evidence that a mixture of magnesium oxide and tricalcium borate has resulted (for the latter compound we referred to the chart No. I/I_1 3-1089 of the collection of *x*-ray data of the *A.S.T.M.*). The conclusion is evident that nocerite cannot have the oxyfluoride composition given to this mineral by previous authors, but must contain boron which apparently has been entirely overlooked by them.

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* We owe two representative samples of nocerite from the original deposits of Nocera, Campania, to the kindness of Drs. C. Frondel (Harvard University), and A. Scherillo (Università di Napoli). To both gentlemen we express our sincere gratitude.

A spectrographic analysis of semi-quantitative character, which we owe to the courtesy of Professor Edward S. Foster, Jr., Physics Department, University of Toledo, has fully confirmed our assumptions by the fact that in the nocerite samples considerable amounts of boron have been identified, besides magnesium and calcium. The fluorine present in the mineral mixture with fluorite is much higher than that which would be combined with calcium in the form of CaF_2. It is therefore concluded that the mineral nocerite is not a simple magnesium borate, like kotoite (cf. T. Watanabe (5)), $3MgO\cdot B_2O_3$, or suanite, (cf. T. Watanabe (6)), $2MgO\cdot B_2O_3$, both from the Hol Kol Mine, Suan, North Korea.

In nature, on the other hand, the existence of a magnesium fluoroborate is well known. It is the mineral called fluoborite, to which is ascribed the general formula $Mg_3(BO_3)_2\cdot 3Mg\,(OH,F)_2$. The compositions given in the literature (cf. Dana's "System of Mineralogy," 7th edition, vol II. 1944, 1951, pp. 369*f*.) differ only in their OH/F ratios. For example this ratio is 1.70 in the fluoborite from the Tallgruvan, Norberg district, Sweden (cf. P. Geijer (7)) but only 0.32 in a fluoborite from Selibin, Malaya (cf. R. W. Johnston and C. E. Tilley (8)), and intermediate, namely about 1.50 in fluoborite from Sterling Hill, N. J. (cf. L. H. Bauer and H. Berman (9), C. Palache (10)). Based on data measured on fluoborite occurrences of different composition, W. T. Schaller, (11) was able to calculate by extrapolation the optical and other constants for the pure F- and OH-end members of the fluoborite series. The calculated data for the pure fluorine fluoborite coincide nearly exactly with those measured by F. Zambonini for nocerite (see Table 1). It is,

TABLE 1

	System	ω	ϵ	Optical Character	Density
Pure F-Fluoborite[1]	hexagonal	1.502	1.487	Negative	2.98
Nocerite[2]	hexagonal	1.5098	1.4855	Negative	2.96

[1] Schaller.

[2] Zambonini.

therefore, plausible to consider that nocerite is identical with pure $Mg_3(BO_3)_2 \cdot 3MgF_2$.

The data given in the literature for the constants of the elementary cell of the Norberg fluoborite (high in OH) are $a_0 = 9.05$ kX; $c_0 = 3.09$ kX (cf. G. Aminoff, in P. Geijer (7)), and for the fluoborite also from Norberg: $a_0 = 9.06$ Å; $c_0 = 3.06$ Å (cf. Y. Takeuchi (12), who gives the space group $C^2_{6h} = C6_3/m$). They are evidently very near to those measured by Scherillo for nocerite (see above). From the x-ray data obtained in our laboratory of the nocerite samples available to us, we calculated the following constants of the elementary cell: $a_0 = 8.82$ Å; $c_0 = 3.10$ Å, in good agreement with those indicated by Scherillo. The slight deviations from the reported data for fluoborite are probably due to the fact that they refer to a crystal phase in which more than half the fluorine is replaced by hydroxyl anions.

The identification of the nocerite sample which we examined, with a mixture of fluoborite and calcium fluoride also easily explains the phenomena observed after heating in open platinum containers in direct contact with the air. Under these conditions the calcium fluoride is evidently gradually changed to calcium oxide which in turn reacts with the fluoborite. Tricalcium borate is the reaction product, and magnesium oxide and magnesium fluoride are set free. Further, the magnesium fluoride is partially changed to magnesium oxide (cf. M. M. Sychev (13).

To confirm our hypothesis here submitted concerning the true composition of nocerite, we synthesized the pure compound $3MgO \cdot B_2O_3 \cdot 3MgF_2$. It is easily prepared by solid state reaction from mixes of the powders of the constituents at a temperature slightly above 1000° C.

In Table 2 the spacings are given for the most important lines of the x-ray powder photographs. For comparison, those of nocerite, of synthetic $Mg_3(BO_3)_2 \cdot 3MgF_2$, and of fluoborite from Sterling Hill, N. J., are tabulated. The identity of the two first patterns is evident. The lines in the third are shifted to smaller 2θ angles, corresponding to the widening effect of the substitution of fluorine by hydroxyl anions. It may also be that the slight differences between the spacings of the nocerite diagram and that of the synthetic pure compound $Mg_3(BO_3)_2 \cdot 3MgF_2$, which are nearly within the limits of error, may be caused by a very small content of OH in the natural nocerite.

CONCLUSIONS

It is concluded that the mineral nocerite originally described as a complex oxyfluoride of calcium and magnesium, with the formula $Mg_3Ca_3O_2F_8$, is in reality a complex fluoroborate of magnesium, con-

TABLE 2

h k l	Nocerite*		Synthetic $Mg_3(BO_3)_2 \cdot 3MgF_2$		Fluoborite from Sterling Hill	
	d(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*
100	7.63	mw	7.60	mw	7.70	mw
110	4.40	m	4.40	m	4.44	m
200	3.82	vw	3.82	vw	3.86	vw
210 101	2.89	mw	2.88	mw	2.92	mw
300 111	2.55	m	2.54	ms	2.56	m
201	2.40	m	2.40	ms	2.42	m
220	2.20	vw	2.19	w	2.22	vw
310 211	2.12	ms	2.12	ms	2.13	m
400	1.911	mw	1.910	mw	1.922	w
221	1.796	m	1.796	ms	1.806	m
320 311	1.750	mw	1.750	m	1.762	mw
410	1.667	w	1.665	w	1.680	w
401	1.625	w	1.626	w	1.638	w
002	1.550	w	1.550	mw	1.558	mw
500 321 102	1.524	w	1.524	mw	1.534	mw
330 411 112	1.466	m	1.466	ms	1.477	m
420 201	1.444	w	1.443	mw	1.453	w

* After deduction of the CaF_2 lines.

taminated by fluorite. It is identical with the synthetic product of the composition $Mg_3(BO_3)_2 \cdot 3MgF_2$ which is the F-end member of the series of complex compounds of the fluoborite group corresponding to the general formula $Mg_3(BO_3)_2 \cdot 3Mg(OH,F)_2$. The term nocerite, therefore, in spite of its evident priority, should be placed into synonymy with fluoborite, this latter name being used for the whole isomorphous series.

ACKNOWLEDGMENTS

We express our gratitude to Dr. C. Frondel who not only furnished us with fine samples of the rare minerals nocerite and fluoborite, but took great interest in our work. He gave us many valuable suggestions for which we are most grateful.

The first-named author feels particularly indebted to the Consiglio Nazionale delle Richerche d'Italia which has given him the opportunity to work, as a Visiting Investigator, for the period from February to July 1956 in the Institute of Silicate Research of the University of Toledo.

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Manuscript received July 25, 1956.

DIAGRAMS FOR THE CORRELATION OF UNIT CELL EDGES AND REFRACTIVE INDICES WITH THE CHEMICAL COMPOSITION OF GARNETS

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The compositions of garnets usually may be expressed in terms of five major components, namely almandite, spessartite, pyrope, grossularite, and andradite. Its other components, such as uvarovite, schorlomite, and hibschite, are of very minor importance. If the chemical composition of the garnet is desired in terms of the five important components, without a chemical analysis, Levin's method (1949 abstract), which determines it from the study of the four physical characters, may be used. However, Levin's procedure requires elaborate calculations, unlike the graphical method here described, by which the result is obtained by direct reading.

Ford (1915) found that one-sixth of all analyzed garnets could be represented by only two components (no other greater than 5 per cent) and two-thirds required three components. Taking three components as significant in a garnet, Kennedy (1947) represented the variation in specific gravity and refractive index with the chemical composition of the garnets. But the specific gravity measurements on the garnet are not always as reliable as the unit cell edge measurements. Skinner (1956) measured the unit cell edges of the end component garnets. Hence the present writer has constructed triangular diagrams (Figs. 1–8) correlating unit cell edges and refractive indices with the chemical composition. By referring the unit cell edge and refractive index, determined by *x*-ray and immerson methods respectively, to these diagrams, the chemical composition can be found in terms of three components of the garnets. Detailed work is in progress to test the diagrams especially with reference to the assumption of the linear variation here made.

My thanks are due to Professors M. P. Billings and C. Frondel for their valuable advice during the progress of this work in the Mineralogical Laboratories of the Harvard University.

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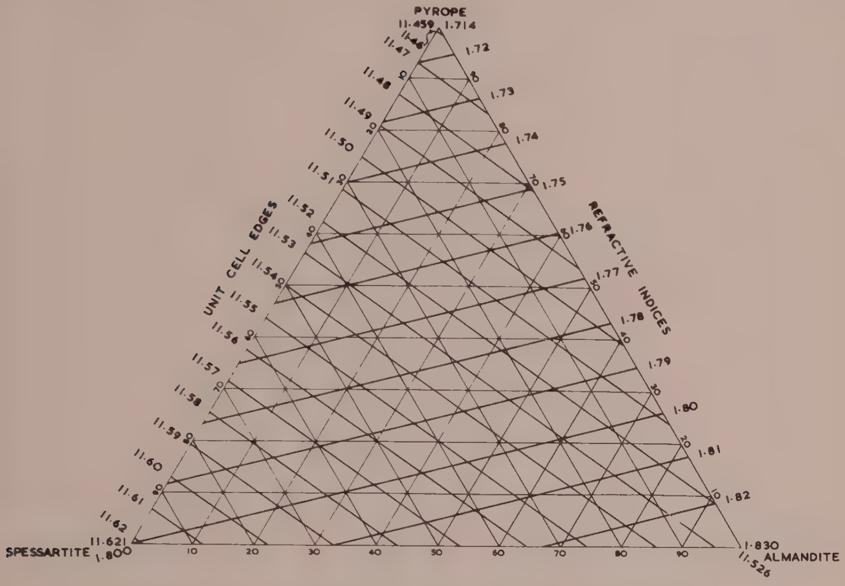

Variation of unit cell edges and refractive indices with chemical composition in the garnet group of minerals.
FIG. 1. Pyrope-spessartite-almandite.

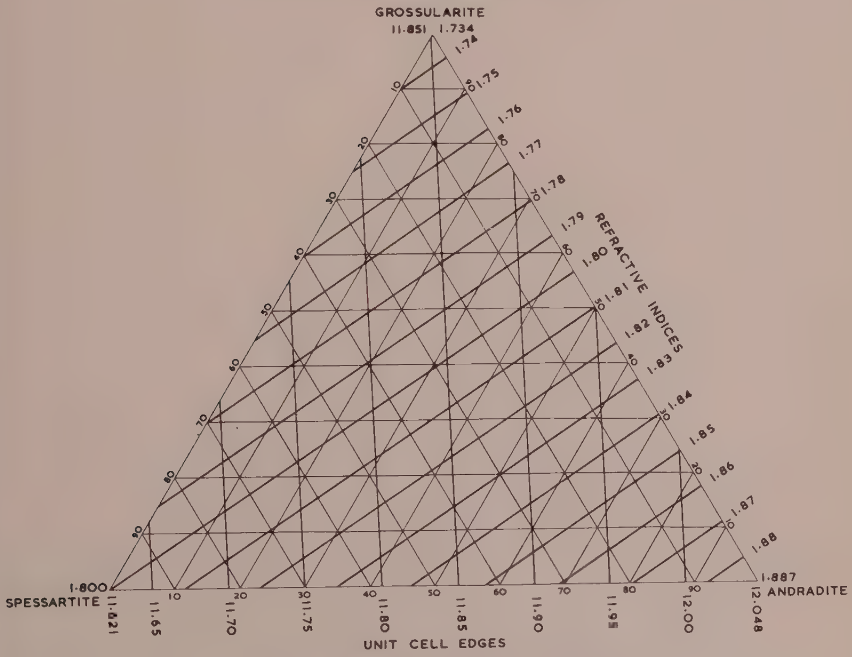

FIG. 2. Grossularite-spessartite-andradite.

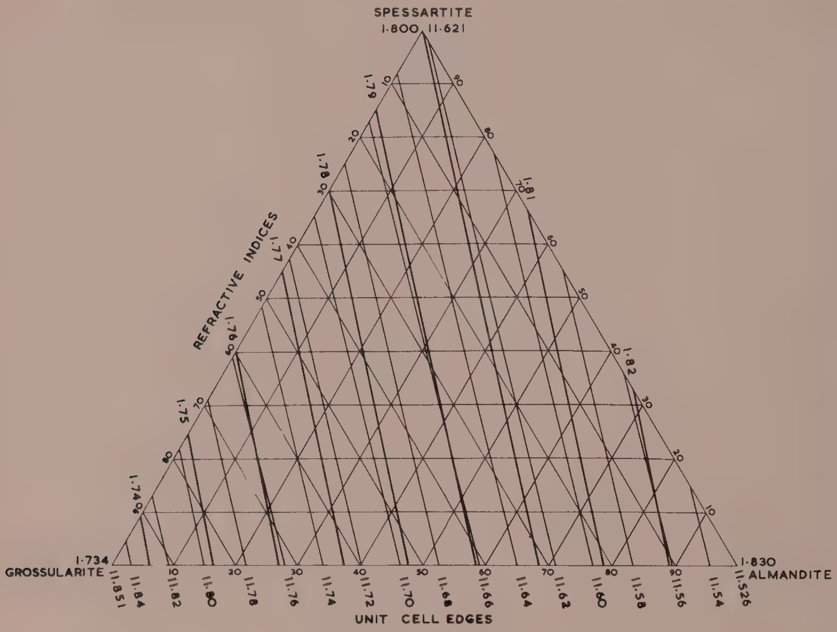

Fig. 3. Spessartite-grossularite-almandite.

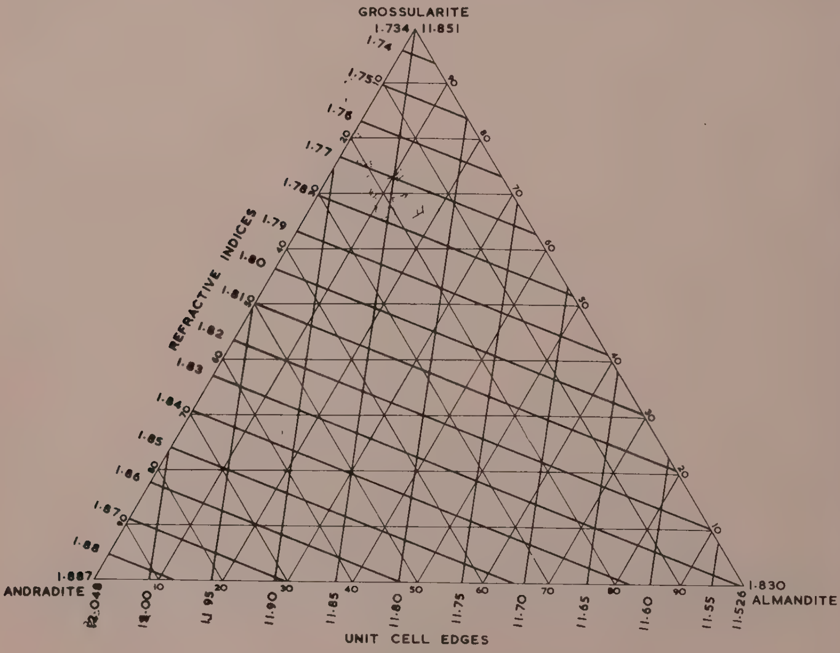

Fig. 4. Grossularite-andradite-almandite.

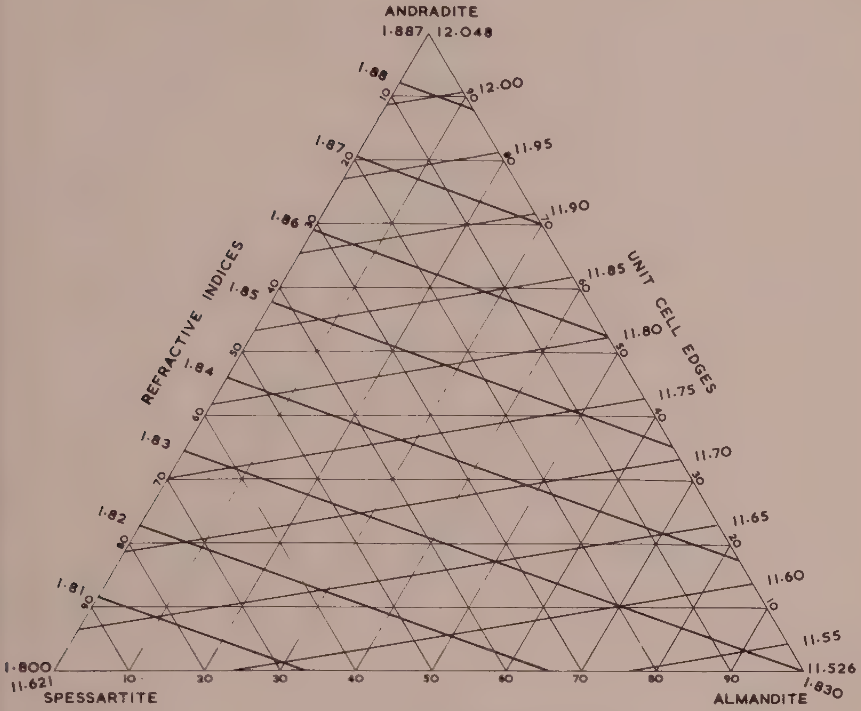

Fig. 5. Andradite-spessartite-almandite.

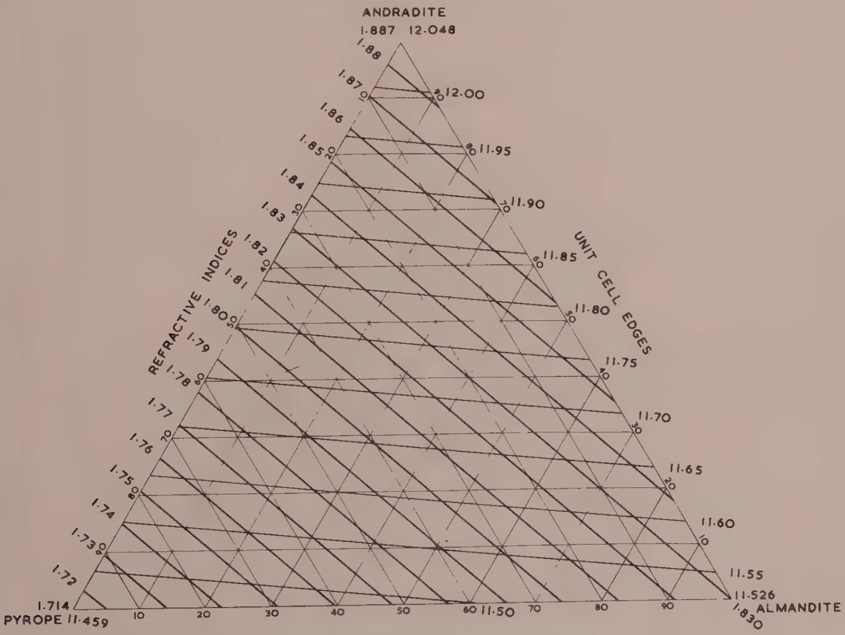

Fig. 6. Andradite-pyrope-almandite.

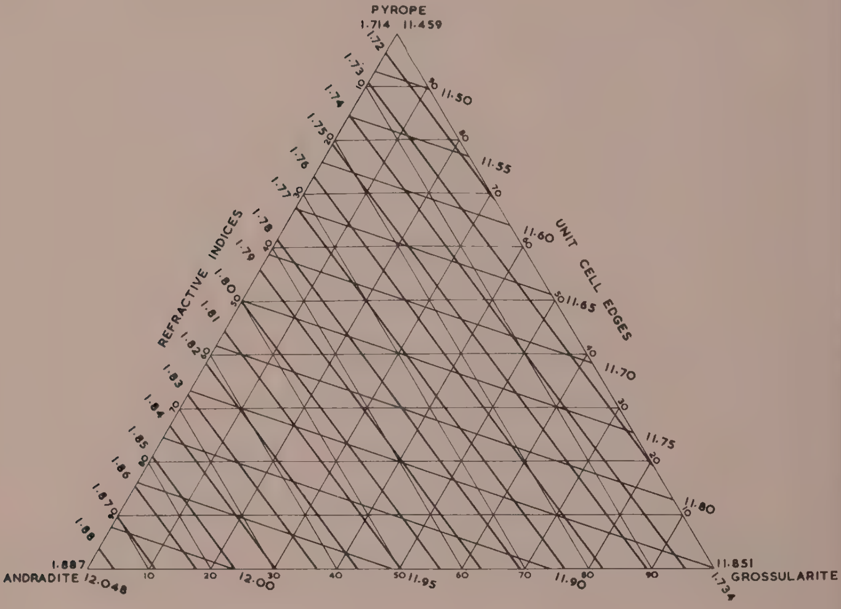

Fig. 7. Pyrope-andradite-grossularite.

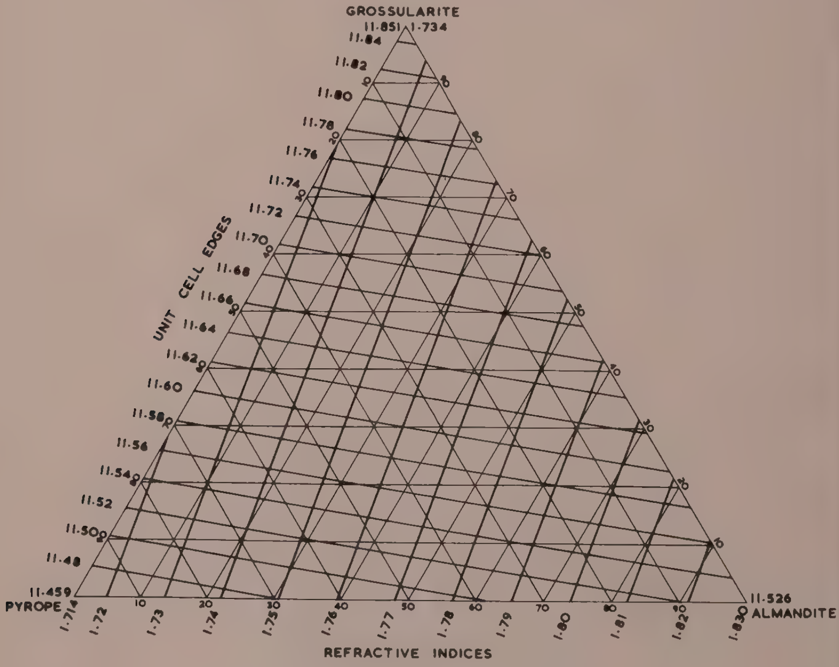

Fig. 8. Grossularite-pyrope-almandite.

HARDNESS OF SYNTHETIC DIAMONDS*

CHESTER B. SLAWSON, *University of Michigan, Ann Arbor, Michigan.*

The hardness tests on synthetic diamond described below were made on a fine diamond grit furnished by the Metallurgical Products Department of the General Electric Company, Detroit, formerly known as the Carboloy Company. Ten carats of grit, minus 325 screen size (<44 microns), were used. By the time rate of settling method a lapping powder, 95% of which was between 15–20 microns, was separated in ethyl alcohol. The coarser particles were crushed and again sized. This was combined with the first fraction and thus the powder tested consisted partly of fine crystals as synthesized and partly of crushed particles. The resulting powder contained a very few of the splinters common to natural powders, which are very difficult to remove by any sizing process.

The hardness of natural diamond increases progressively in the zone from (101) to (111), from its lowest value, which is on (101), to its highest value, that on the octahedron face, provided the lap moves in the direction from (111) to (101) (Denning, 1953). This gives an angle of 35°16′ through which a diamond may be turned with a progessive increase in hardness. Fig. 1*a* shows an octahedron in the position of greatest ease of cutting, Fig. 1*b* in the position in which it is impossible to cut because none of the randomly oriented diamond particles on the lap can be harder than this direction. In commercial practice 3° from the octahedron is considered the closest a facet in this zone can lie to the octahedron and still be cut and effectively polished.

A nearly perfect gem quality natural two and one-half carat diamond with a faint tinge of yellow was abraded on a new lap, freshly charged with the prepared synthetic diamond powder. Diamonds of this type with a faint yellow tinge rarely show internal twinning laminations which would introduce a disturbing factor into the test. No evidence of twinning was observed on the natural octahedron that was used in this test (Slawson, 1950). The synthetic powder readily cut and polished a facet on the natural crystal which lay 3° off the octahedron. After progressively approaching closer to the octahedron a position was arbitrarily chosen as the practical limit of cutting. A good polish was still produced. Subsequent measurement showed that this facet was within 1°23′ of parallelism with the octahedron. This procedure is a very sensitive method of comparing relative hardness.

If a diamond is cut in the softest direction, Fig. 1*a*, the material removed becomes imbedded in the surface of the lap and assists in the further cutting on that lap. In this test the natural octahedron was placed on the charged lap for the first time in a position 3° from parallelism with the lap, in other words, close to the position shown in Fig. 1*b*. After an interval of 10 seconds an observable facet was cut. Standard equipment and procedures of gem diamond cutters were followed, except for a special solder dop that allows small angular changes in the position of the diamond on the lap to be made with adjusting screws. The preparation of the synthetic powder and the testing was done by the writer, with financial support from the Office of Naval Research.

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* Contribution from the Department of Mineralogy, University of Michigan, No. 210.

One concludes that there is no difference in the actual hardness of natural and synthetic diamond. It is believed that the slightly better value and the more rapid rate of abrasion by the synthetic powder can be attributed to the mechanical superiority of the research prepared powder and to its freedom from elongated cleavage splinters. No natural powder was prepared for comparative tests because no appreciable amounts of minute natural crystals were available. Crushing of larger crystals always produces splinter cleavage fragments.

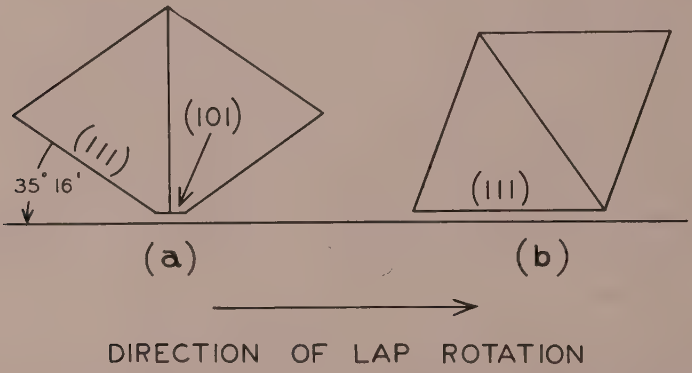

Fig. 1. Grinding hardness in diamond, (a) softest direction, (b) hardest direction.

The conclusion that synthetic and natural diamond are of the same hardness was anticipated because *x*-ray diffraction patterns and close microscopic examination revealed no significant differences. A very few faint lines of an unknown impurity were observed on some *x*-ray powder patterns of the synthetic diamond.

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BORAZON

In view of the somewhat inadequate newspaper reports concerning the production by the General Electric Co. of cubic boron nitride, the following information has been obtained from the official report.

It is in the same general range of hardness as diamond; borazon scratches diamond, and diamond scratches borazon. In actual lapping tests, borazon powder polished a diamond at the same rate as diamond powder. But in another important characteristic, borazon appears superior. Diamond, being carbon, burns in air at about 1600° F. Borazon can withstand temperatures of more than 3500° F.

The material produced consists of tiny crystals no larger than grains of sand, and is generally black, brown, or dark red, although milky white, gray and yellow crystals have been made.

Pressures above one million pounds per square inch and temperatures exceeding 3000° F. are used to produce crystals of boron nitride with a structure that is not hexagonal like graphite, but cubic, like diamond. *X*-ray diffraction tests of borazon reveal that the alternate atoms of B and N are packed almost as closely as the C atoms in diamond. The specific gravity is also about the same: 3.45 for borazon; 3.50–3.56 for diamond.

Notice Concerning Decennial Index, 1946–1955

The ten year index for volumes 31 to 40 of *The American Mineralogist* is now in preparation. As in previous issues, this will include a list of Errata. Readers are urged to report any errors which they have detected that have not already been corrected in subsequent numbers. Send to Dr. Earl Ingerson, U. S. Geological Survey, Washington 25, D. C.

Note to Authors

When authors submit papers describing investigations in which *x*-ray powder measurements were made, but omitting the actual *x*-ray data, it is requested that these data be submitted to the Editor of the Joint Committee on Chemical Analysis by Powder Diffraction Methods for possible inclusion in the "*X*-ray Powder Data File," published by the A.S.T.M.

The data should contain accurate listings of "*d*" values and intensities of reflections. Other items of information of value for the data file are: *hkl* indices and lattice parameters if known, radiation used, type of *x*-ray recording employed, method of estimating intensities (visual, photometric, geiger-counter), plus any relevant information concerning the nature and preparation of specimens studied.

G. W. Brindley
Editor, "*X*-ray Powder Data File"
College of Mineral Industries
The Pennsylvania State University
University Park, Pennsylvania, U.S.A.

Dr. William T. Pecora has replaced Dr. Earl Ingerson as Chief, Geochemistry and Petrology Branch, U. S. Geological Survey. Dr. Ingerson was at his own request relieved of administrative responsibilities in order to devote full time to research.

It is with deep regret that we report the deaths of several prominent mineralogists.

František Slavík, Correspondent of our Society, and Professor-emeritus of Mineralogy at Charles University, Praha, Czechoslovakia; January 27, 1957, at the age of 80.

George D. Louderback, Fellow, and Professor-emeritus of Geology at the University of California, January 29, 1957, at the age of 82.

Brenno Wasserstein, Fellow, December 12, 1956. Dr. Wasserstein had just come from South Africa to the United States to set up a mineral research laboratory at Oakland, California.

Memorials of these members will appear in a later issue.

Kurt Spangenberg, Professor of Mineralogy and Director of the Mineralogical Museum, University of Tübingen, January 25, 1957.

Apparently damage occurred to a sack of mail going to southern California, which contained copies of the January–February issue of *The American Mineralogist*. Members who failed to receive this issue, or who received a damaged copy, may write to the editor for a replacement.

Sixth Annual Conference on Industrial Applications of X-ray Analysis

The technical sessions of this conference, sponsored by the Metallurgy Division, Denver Research Institute, University of Denver, will be held August 7, 8 and 9, 1957, followed by a mountain tour on August 10. Deadline for titles and authors May 1; deadline for abstracts, June 1, 1957. For further information write to

James P. Blackledge, *Head, Metallurgy Division,*
Denver Research Institute, University of Denver

The 27th annual meeting of the Society of Exploration Geophysicists will be held at the Statler-Hilton Hotel in Dallas, Texas, November 11–14, 1957.

The 7th annual convention of the Eastern Federation of Mineralogical and Lapidary Societies will be held August 29–31, 1957, at the Chamberlin Hotel, Old Point Comfort, Virginia, with the Gem and Mineral Society of the Virginia Peninsula acting as host. There are plans to cooperate with the Jamestown Festival.

A collection of Chinese jade, one of the largest and most valuable ever shown in America, will be on display this spring in the Pioneer Museum and Haggin Galleries in Stockton, California. Open to the public without charge.

Professor E. Wm. Heinrich, Department of Mineralogy, University of Michigan, has been appointed editor of *The Geochemical News*, the official news letter of the Geochemical Society.

The 7th Colloquium Spectroscopicum Internationale will take place in Liege, Belgium, in the second week of September, 1958. It will be organized by the Association of Engineers of the Liege University (A.I.Lg.) with Professor L. D'Or as chairman. The address of the secretary is

VII Colloquium Spectroscopicum Internationale Association des Ingénieurs
de l'Université de Liège, A.I.Lg., *22, rue Forgeur, Liege, Belgium.*

BOOK REVIEWS

BIBLIOGRAPHY OF HARDNESS AND HARDNESS TESTING. 118 pp., name and subject indexes, offset-lithographed, 1955/1956, Industrial Diamond Information Bureau, London E.C. 1. Price 5s. 6d.

The Bibliography of Hardness and Hardness Testing from 1937 to 1955 includes published material on the subject of hardness testing, applied and fundamental. The compilers of this bibliography intend to give the worker in the field of hardness, and in particular microhardness, a tool which will enable him to obtain up-to-date information on any particular branch or aspect of hardness, or to compare his own work with that of others. Items are listed as follows:

A. Books, brochures, and bibliographies, 1822–1955 (7 pages).
B. National Standards (4 pages).
C. Publications in Technical Journals, 1937–1955 (78 pages).

Two indices, a name index including proprietary names, and a subject index are useful.

Symbols are given which indicate the general scope of the entries. English translations of French and German titles are given in addition to the original titles. Russian titles are given in English translation only. Publications from a large variety of journals are included, mechanical, metallurgical, chemical, and ceramic engineering, mineralogical, geological, and others.

The papers from these journals are listed according to year and also alphabetically by author within the year.

The magnitude of the task is so great that errors of omission are almost a foregone conclusion at the outset. The reviewer noted the absence of a number of papers in the field of diamond hardness, namely, Bergheimer (1938), Whittaker and Slawson (1946), Slawson and Kohn (1950), Hukao (1953), Denning (1953, 1955). Kohn's paper on silicon carbide (1951) was omitted, as also was Winchell's (1946) paper on orientation and hardness variation. (These references are given below.)

The failure to include these publications in the bibliography would lead one to question whether omissions might be numerous in other fields of hardness investigation. Nevertheless, the work constitutes a significant collection of references which are widely scattered through an unusually large variety of literature. All persons engaged in research in practical hardness testing methods, as well as those engaged in the theoretical aspects of the study of hardness, should find this bibliography invaluable.

References

Bergheimer, H. (1938), Die Schleifhärte des Diamanten und seine Struktur: *Neues Jahrb. Min. Geol. und Pal.*, **74,** 318–332.

Denning, R. M. (1953), Directional grinding hardness in diamond: *Am. Mineral.*, **38,** 108–117; reprinted *Ind. Diamond Rev.*, **13,** 175–182.

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Hukao, Y. (1953), Abrading tests of diamond: *Ind. Diamond Rev.*, **15,** 45–48; 107–109.

Kohn, J. A. (1951), Directional variation of grinding hardness in silicon carbide (SiC): *Ind. Diamond Rev.*, **11,** 211–212, 235–237.

Slawson, C. B., and Kohn, J. A. (1950), Maximum hardness vectors in the diamond: *Ind. Diamond Rev.*, **10,** 168–172.

Whittaker, Harry, and Slawson, C. B. (1946), Vector hardness in diamond tools (Third Symposium on Diamonds): *Am. Mineral.*, **31,** 143–149.

Winchell, H. (1946), Observations on orientation and hardness variations (Third Symposium on Diamonds): *Am. Mineral.*, **31,** 149–152.

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DIAMOND—The Spectacular Story of Earth's Rarest Treasure and Man's Greatest Greed, by Emily Hahn. 314 pp., Doubleday and Co., Inc., Garden City, New York, 1956. Price, $3.95.

Although the author was graduated from the University of Wisconsin in 1926 as a mining engineer, she has devoted much time to activities which have involved extensive travels the world over and is widely known as a prolific author of articles and books of general interest. It is estimated that she traveled over 20,000 miles to gather material for this book—DIAMOND—much of which originally appeared in the *New Yorker.*

In nine chapters—Kimberley, Old Digger-Old Fool, The Giants, The Premier, And Son, The Cutters, The Shade of J. Ballantine Hannay, Staring at Stones, and Paradise-Limited—the results of her interviews with many of the present leaders in the mining, cutting, and marketing of gem and industrial diamonds are discussed in a style which appeals to the general reader. Throughout, an attempt is made to piece together the history of the discovery and recovery of diamonds in Africa and to present interesting and some not well known facts of the activities and characteristics of such leaders as Cecil Rhodes, Barney Barnato, Sir Ernest Oppenheimer and his brothers, as well as of many others. The book is of general rather than of scientific interest to those who desire information about the diamond. There is a selected bibliography and an index. There are no illustrations in the book.

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LAS ESPECIES MINERALES DE BOLIVIA, by Federico Ahlfeld and Jorge Munoz Reyes, 180 pages. Banco Minero de Bolivia, La Paz, 1955. Price $3.50*

Although there is no indication of the fact on cover or title page, the current volume is essentially a third edition, two earlier works by the same authors having appeared with slightly different titles: Mineralogía Boliviana (1937) and Los Minerales de Bolivia (1943). The first of these was translated into German (Mineralogie von Bolivien, Gebruder Borntraeger, Berlin, 89 pages, 1938; see *Am. Mineral.*, **23,** p. 538, for review) and probably enjoyed a greater circulation than either of the Spanish versions.

There are essentially twice as many pages in this edition as there were in the first, although the species described have increased only 42% (From 170 to 242 definitely identified; in an appendix six more doubtful species and several unidentified ones are briefly mentioned, but not numbered). The increased number of pages, therefore, is due in large measure to more detailed treatment of individual species. Cassiterite, for example, has five pages and four crystal drawings in the 1938 publication, but is given eight pages, 18 crystal drawings, three photomicrographs, and one picture of a hand specimen in the volume under review. This increase in illustrations is reflected throughout the book, with 121 crystal drawings against 30 in the earlier edition and 16 photographs and photomicrographs as compared with two pictures before. There are 129 literature references whereas the first edition had 75.

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* Can be ordered from Dr. Federico Ahlfeld, Naciones Unidas TAA Casilla 686, LaPaz, Bolivia.

The mineral descriptions are concise with more emphasis on distinguishing characteristics and localities of Bolivian minerals than on general characteristics, these latter being confined commonly to a brief introductory paragraph in fine print.

No attempt is made to multiply the mineral species that occur in Bolivia. Only the ones that have been positively identified are described. Of the rock forming minerals only the more important ones are treated, and these very briefly. For example, only three feldspars are mentioned and these are disposed of in slightly over one page. Agate, chalcedony and other varieties of silica (except opal and tridymite) are treated under quartz.

There are complete indices of minerals of economic interest, arranged by elements, and of localities, as well as one of mineral species listed alphabetically. The book is a very attractive, well-printed and usable compendium of information on Bolivian minerals and mineral localities.

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CLAYS AND CLAY MINERALS, EDITED BY ADA SWINEFORD. *National Academy of Sciences, National Research Council Publ. 456,* viii+444, Washington, D. C., 1956, $6.00. (*Proc. 4th Natl. Conference on Clays and Clay Minerals, University Park, Pa., Oct. 10–13, 1955.*)

About a third of the papers in this volume were contributed by foreign scientists. Although some of these articles are quite specific as to topics discussed, others are so general in nature as to lead merely to the conclusion that clays and scientists investigating clays are widely distributed geographically. This conclusion, to be sure, is not very profound, but neither are several of these papers.

A twenty-page guide to the field trip is followed by 46 papers (or abstracts in a few cases) and a general index. Discussions, which may be more interesting and even more informative than the scheduled contributions, were not recorded for this conference.

Several corrections have come to this reviewer's attention: legends for Figs. 2 and 3 (pages 33, 34) are transposed; for Figs. 2, 3 and 4 (pages 129–130) the curves are for metametahalloysite (top), metakaolinite and metadickite (bottom); Fig. 5 (p. 131) curves are for kaolinite (Pugu), halloysite, dickite, nacrite and kaolinite (top to bottom). "Wolchonskoite" is something betwixt and between German and English. Although "puguite," a term used orally at the conference, might have some onomatopoeic value, this reviewer—and probably several other persons—was pleased to find it had got lost before the recording of these proceedings.

As is true of earlier publications of this series, this document will be essential to the libraries of certain ultra-ultraspecialists as well as all mineralogists who attempt to keep informed on clay minerals.

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ELEMENTARY CRYSTALLOGRAPHY (AN INTRODUCTION TO THE FUNDAMENTAL GEOMETRICAL FEATURES OF CRYSTALS), BY M. J. BUERGER. John Wiley and Sons, Inc., New York, 1956, xxiii+528 pp., 610 figs., 6×9 in. Price $8.75.

In the preface to the first edition of the well-known book "An Introduction to Crystallography," the author, F. C. Phillips, states "text-books of science, in the mind of the discerning critic, usually fall readily into one or the other of two groups, the helpful and the impressive, accordingly as the author's outlook is directed mainly toward the reader's progress or towards the enhancement of his own reputation." In the case of the book under review here, it is clear that notwithstanding the fact that the author's outlook is "directed mainly towards the reader's progress," he has in spite of himself added appreciably to an already considerable reputation in the scientific community by its writing.

The book is concerned solely with the symmetry properties of crystals and with some of the physical manifestations of these properties. The mathematical theory of the symmetry operations possible for crystals is developed in considerable detail. In this development the author has made every effort to avoid the use of complicated mathematics and at the same time to maintain rigor; because of this some of the exposition is necessarily lengthy. Perhaps the most satisfactory way of handling the mathematical treatment of symmetry operations is with the concise and elegant method of group theory. The author uses the notation and ideas of group theory informally throughout the book, without identifying these as such. In the last three chapters he presents a formal unified discussion of the elementary theory of groups as applied to symmetry operations. Roughly half the book is devoted to a discussion of the megascopically observable symmetries of crystals; the other half discusses the internal symmetries. The purely geometrical aspects of the crystal are related to the physical aspects in a most effective manner, in three excellent chapters. These are Chapter 10, "Crystal Forms," Chapter 11, "Practical Determination of Point-Group Symmetry," and Chapter 19, "The Determination of Space-Groups and the Utilization of Space-Group Information."

In keeping with the text-book aspect, most of the chapters are followed by a small number of exercises. The numerous line drawings, so necessary to a book on the subject of crystallography, have been carefully thought out and executed. There are a large number of useful tables. The general format of the book is up to Wiley's usual high standards: the type is very readable and particularly effective use has been made of varying type face.

With regard to the use of the word "elementary" in the title, the book is elementary in the sense that it presents the elements—the fundamentals of crystallography, namely, the theory of symmetries of crystals. It is also elementary in the sense that every attempt has been made to develop the subject in such a way that the minimum prior knowledge of crystallography is necessary on the part of the reader.

Previous to the publication of the present book there existed in print no modern, extended, elementary (in the usual sense) treatment of the symmetries of crystals. It will, therefore, be used not only by the student but will be welcomed by the practicing crystallographer in general.

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NEW MINERAL NAMES

Boltwoodite

Clifford Frondel and Jun Ito, Boltwoodite, a new uranium silicate. *Science*, 124, No. **3228,** p. 931 (1956).

Analysis of a small sample containing brochantite and small amounts of unidentified impurities gave SiO_2 12.74, UO_3 58.68, K_2O 8.03, Na_2O 0.33, CuO 9.61, SO_3 2.12, H_2O 7.33, insol. 0.19, not detd., (Al_2O_3, CaO, MgO, PbO, V_2O_5) 0.34, sum 99.37% (given as 99.88% in original M. F.). This yields, after deducting brochantite, $K_2(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$. The mineral is yellow, fibrous. Optically biaxial, neg. nX 1.668, nY 1.696?, nZ 1.703. Extinction parallel. Pleochroism weak, X colorless, Y and Z yellow. Orthorhombic or monoclinic with the fiber elongation along the *b*-axis. G. about 3.6. Weakly fluorescent in dull green under both long- and short-wave excitation. The *x*-ray pattern suggests a structural relation to sklodowskite. The strongest lines are (in Å) 6.81 10, 3.39 8, 2.94 8, 3.53 7, 2.89 6. The mineral occurs at the Delta Mine (Pick's Mine), Emery County, Utah, in wartlike aggregates of fibers coating fractures in sandstone. It is an oxidation product of primary black ores. Associated minerals are brochantite, becquerelite, gypsum, and coarse golden fibers of an unidentified uranyl silicate.

The name is for Bertram B. Boltwood (1870–1927), pioneering radiochemist, of Yale University.

Michael Fleischer

Lodochnikite (Lodochnikovite), Ufertite (Uferite), Obruchevite

On p. 825 of vol. 6 (published 1956) of the *Conference on Peaceful Uses of Atomic Energy, Geneva, 1955*, are remarks by Mr. Melkor of the U.S.S.R. delegation, in which he gives a list of new uranium minerals. Some of these were previously abstracted (*Am. Mineral.*, **41,** 816 (1956)). The following additional names are given by Melkor (M.) and are also mentioned in a paper on Uranium Minerals by V. I. Gerasimovsky (G.) in *Atomnaya Energiya* No. **4,** 118–130 (1956).

Lodochnikovite (G.), Lodochnikite (M.)—$2\,(U, Th)O_2 \cdot 3UO_3 \cdot 14TiO_2$. In hydrothermal veins. Names for the Soviet petrographer B. N. Lodochnikov.

Note: This is not the same mineral as that previously described under the name lodochnikovite, see *Am. Mineral.*, **40,** 551 (1955), **41,** 672 (1956).

Ufertite (M), Uferite (G.)—$20\ FeO \cdot 8\ Fe_2O_3 \cdot 4\ TR_2O_3 \cdot UO_2 \cdot 74\ TiO_2$.

Obruchevite—$(Y, U, Na_2)Ta_2O_6\ (OH,F)$ Named for the Soviet geologist V. A. Obruchev.

The names given in the French publication abstracted in *Am. Mineral.*, **41,** 816 (1956) agree with those listed in the English brochure describing the Soviet exhibit. The two more recent publications show two changes:

The name prjevalskite is spelled przhevalskite and the name priguinite is spelled iriginite. The composition of orlite, previously given as $3PbO \cdot 3UO_3 \cdot 4SiO_2 \cdot 6H_2O$ is given by G. as $Pb_3(UO_2)_3Si_2O_7 \cdot 6H_2O$ with 43.57% UO_3 (formula doesn't balance. M. F.).

M. F.

Smolianinovite

L. K. Yakhontova, A new mineral—smolianinovite. *Doklady Akad. Nauk S.S.S.R.*, **109,** 849–850 (1956) (in Russian).

The name is given to a yellow, earthy oxidation product of nickel and cobalt arsenides. Four analyses led to the formula $(Co, Ni, Ca, Mg)_4(Fe^{III},Al)_2(AsO_4)_4O \cdot 11H_2O$ (which could be written (Co, Ni, Ca, Mg)$_4$(Fe,Al)$_2$(AsO$_4$)$_4$·10H$_2$O—M.F.). In the analyses, CoO ranges from 8.01 to 9.02, NiO 6.17 to 9.19, CaO 3.44 to 4.81, MgO 2.16 to 3.22%. (The formula as given includes only H_2O^+; if the H_2O^- is included, the first formula above would have 15H$_2$O. M.F.). A dehydration curve shows continuous loss of water up to about 320°. The mineral is in earthy to dense aggregates of finely fibrous material. Luster silky. Hardness about 2. Sp. gr. 2.43–2.49. Extinction parallel, elongation positive, birefringence about 0.006–0.008, mean *n* 1.625 ± 0.005. *X*-ray powder patterns showed only 3 broad lines at 10.87, 3.16, and 2.88 Å, with intensities 10, 7, and 6.

The mineral is widely distributed as an oxidation product of smaltite, safflorite, and rammelsbergite. The only locality mentioned is Bou-Azzer, Morocco.

The name is for Professor N. A. Smolianinov, Russian mineralogist.

Discussion—If all the Fe$_2$O$_3$ is calculated as FeO, the analyses give $R_3(AsO_4)_2 \cdot 7\frac{1}{2}H_2O$, which suggests that the mineral may be an oxidation product of annabergite-erythrite that contained some FeO. However, no analyses of annabergite or erythrite show this much FeO.

M. F

Vinogradovite

E. I. Semenov, E. M. Bohnshtedt-Kupletskaya, V. A. Moleva, and N. N. Sludskaya, Vinogradovite—a new mineral. *Doklady Adak Nauk S.S.S.R.*, **109**, No. **3**, 617–620 (1956).

Analyses from Takhtarvumchorr, Khibina, and from Nepkha, Lovozero, gave SiO$_2$ 40.70, 40.83; TiO$_2$ 33.60, 35.86; Al$_2$O$_3$ 6.20, 4.88; MgO 0.36, 0.42; CaO 1.00, 0.66; Na$_2$O 12.00, 10.39; K$_2$O 1.78, 2.10, H$_2$O (total) 4.80 (H_2O^- 0.66), 5.50, sum 100.44, 100.64% (V.A.M., analyst). Nb was found by *x*-ray spectroscopic analysis; a sample from Mannepakhk contained 3.52% Nb$_2$O$_5$. Spectrographic analysis showed the presence of 0.08% BeO; other samples contained up to 0.2% BeO. Qualitative spectrographic analysis showed also Fe, Mn, Sr, Ga, and Zr (weak lines). The analyses yield approximately the formula $Na_5Ti_4AlSi_6O_{24} \cdot 3H_2O$. (They give more closely (Na, Ca, K)$_4$Ti$_4$AlSi$_6$O$_{23}$(OH)·2H$_2$O. M. F.). The mineral dissolves in acids on heating. A dehydration curve is given; most of the water is given off at 200–500°.

Vinogradovite occurs in spherulites and in aggregates of fibrous crystals, less commonly in cavities as fine prismatic crystals showing the faces *b* (010), *m* (110), *n* (410), *d* (101), and *D* ($\bar{1}01$). Goniometric data gave approximate measurements (poor signals) yielding $a:b:c = 1.18:1:0.76$, beta 91°58′. The monoclinic, pseudo-orthorhombic character was verified by Laue diagrams. *X*-ray powder data are given for the analyzed samples; the strongest lines (d in Å and intensities) are 3.21, 3.20, (10,10); 3.07, 3.05 (10,10); 1.614, 1.618 (8,8); 2.72, 2.71 (7,7); 1.558, 1.562 (7,6); 1.494, 1.494 (7,6); 1.434, 1.438 (7,6); 2.48, 2.47 (6,7); 2.56, 2.58 (6,6).

Vinogradovite is colorless to white with vitreous luster. Brittle, cleavage (010) perfect, fracture uneven. Hardness about 4. Specific gravity 2.878. Before the blowpipe fuses easily (about 800° C.) to a bluish-gray opaque bead. Optically biaxial, negative, with *N*s alpha 1.745, beta 1.770, gamma 1.775, 2V 41°, *c:* gamma 7°, elongation positive; the plane of the optic axis is perpendicular to (010). Sometimes weakly pleochroic from colorless on X to brownish on Z. Dispersion $r > v$.

Found at 12 localities in nepheline syenite pegmatites of the Khibina and Lovozero massifs, Kola Peninsula, in cavities of natrolite or analcime in the central part, or replacing ramsayite and lamprophyllite in the contact zone.

The name is for Alexander Pavlovich Vinogradov, Russian geochemist.

M. F.